

Intrinsic physicochemical activity at microplastic–water interfaces

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Plastics have become an integral part of our modern society, largely because they are generally regarded as chemically inert under normal circumstances. However, plastics fragmented into microplastics (less than 5 mm in size) have recently raised significant public concerns, and have been detected widely across ecosystems and human tissues with increasing environmental and health risks^{1–5}. Here we show that commodity microplastics exhibit intrinsic physicochemical activity in water, manifested by the spontaneous generation of reactive oxygen species that increases with interfacial hydrophobicity and strongly correlates with interfacial electrostatics. *Ab initio* calculations support these observations and reveal that hydroxide oxidation becomes energetically more favourable at increasingly hydrophobic microplastic–water interfaces through the combined effects of partial solvation and electrostatics. These interfacial properties and the resulting oxidative chemistry have direct implications for biomolecular adsorption, protein aggregation, and even cellular damage. Together, our findings challenge the prevailing paradigm of plastic inertness, identify a possibly overlooked mechanism for the detrimental effects of microplastics on health and the environment, and contribute to a fundamental understanding of the structure–activity relationship of interfacial water, which may inform the design of safer and more sustainable plastic materials.

Commodity plastics are valued for their durability, chemical resistance and broad utility. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA) and polyethylene terephthalate (PET) are widely used across many industries. Their extensive use rests in part on the prevailing view that plastics are largely inert under ordinary conditions and therefore safe for general use. In particular, polyolefins such as PP and PE, composed of only non-polar hydrocarbon chains, are known for their durability and chemical resistance.

Apart from their bulk form, however, plastics also exist as micro- and nanoplastics (MNPs), which are raising public concerns with their presence detected in almost every corner of our world¹, and even inside human bodies². Mounting evidence suggests that micro- and nanoplastics can impose adverse health consequences on biological systems, inducing stress, inflammation and cytotoxicity in various model systems from cells to higher organisms^{4,6}. Human epidemiological studies further reveal a surprisingly high correlation of exposure to micro- and nanoplastics with reproductive damage⁷, cardiovascular problems³, neurological diseases⁵, inflammatory bowel disease⁸ and cancer⁹, raising broad concerns about their health consequences. Although the molecular mechanisms remain elusive and are probably multifactorial,

plastic composition, particle morphology and shape, and surface functionalization all have a role in how microplastics interact with biological systems and induce toxicity¹⁰.

The presumed chemical inertness of bulk plastics needs to be reconciled with the toxicity of their fragmented microscale forms. Plastics in nature are in constant contact with water, organic matter and air, making the plastics–environment interface a potentially important but underappreciated determinant. Moreover, the prevailing notion of plastic inertness largely derives from their behaviour as bulk materials. Fragmentation into microplastics greatly increases the surface-to-volume ratio, potentially amplifying any plastic–environment interfacial activity and endowing microplastics with emergent activity that is inconsequential in the bulk state.

Motivated by these considerations, we sought to test the prevailing paradigm of plastic inertness by investigating their interfaces with the environment. Using a suite of complementary analytical techniques across a series of commodity plastics, we observe prolific hydroxyl radical ($\bullet\text{OH}$) generation at increasingly hydrophobic microplastic–water interfaces, accompanied by strong interfacial electrostatics that correlate with radical generations. Molecular simulations and *ab initio* calculations further reveal a structure–activity relationship linking

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microplastic surface chemistry to interfacial water, in which partial solvation and electrostatic effects together render $\bullet\text{OH}$ generation near hydrophobic microplastic–water interfaces. This intrinsic physicochemical activity provides a functional hypothesis for understanding how microplastics may interact with, chemically modify, and even damage biomolecules and cells.

Importantly, this activity arises from fundamental water–hydrophobe interactions, including interfacial water restructuring, electrostatics and partial solvation. These features closely parallel those implicated in the emerging field of microdroplet chemistry, where water interfaces have been shown to accelerate diverse reactions and promote redox processes that are otherwise unfavourable in bulk water^{11–30}. By analogy, the widespread and persistent hydrophobic surfaces created by fragmented microplastics may serve as an alternative, solid-supported platform for analogous interfacial chemistry, with implications across material, biomedical and environmental sectors.

Spontaneous radical generation at the interface

PS, one of the most common commodity plastics, contains no reactive functional groups beyond its hydrocarbon backbone and pendant phenyl groups, and is known for its chemical resistance and durability. Methyl orange, an azo dye, is susceptible to degradation by reactive oxygen species (ROS)³¹. Because PS powder is poorly soluble in water and generally regarded as chemically inert, PS microplastics are not expected to chemically interact with methyl orange. However, we observe unexpected methyl orange degradation when PS microplastics are mixed with water containing methyl orange. Although methyl orange remains stable in solution without PS, continuous stirring with PS microplastics causes methyl orange degradation with a progressive colour change from light yellow to nearly colourless over 10 days (Fig. 1a,b). Strikingly, no comparable methyl orange degradation is observed when PS is suspended or dissolved in other common solvents containing methyl orange (Fig. 1a,c and Extended Data Fig. 1a). The nearly 90% degradation observed exclusively in water therefore highlights a critical role of the aqueous solvent in transforming otherwise inert PS microplastics into chemically active particle suspensions.

To determine whether ROS are generated from PS microplastics in water, we use electron spin resonance (ESR) spectroscopy. Using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a radical trapper, we detect a mixture of different radical species generated upon dispersing PS microplastics into water (Fig. 1d). The dominant feature of ESR spectra is a sextet signal attributed to oxidation of DMPO to an epoxy hydroxylamine ($\text{HDMPO}=\text{O}$) intermediate, which can subsequently react with a $\bullet\text{OH}$ to generate an ESR-active radical ($\text{DMPO}=\text{O}\bullet$)³². Direct trapping of $\bullet\text{OH}$ is also detected as a weaker component of the ESR spectrum (Fig. 1d). As $\bullet\text{OH}$ is known to cleave the azo bond³³, the presence of $\bullet\text{OH}$ in the water containing PS microplastics explains the observed methyl orange degradation therein.

To examine whether highly reactive radicals originate at the PS surface, we use aminophenyl fluorescein (APF), a fluorogenic sensor with high specificity for $\bullet\text{OH}$, to image its *in situ* generation by confocal microscopy (Fig. 1e and Extended Data Table 1). Spatial mapping of the fluorogenic reactions shows fluorescence localized predominantly at the particle surface, supporting an interfacial origin of $\bullet\text{OH}$ generation (Fig. 1f). The reactivity at the PS–water interface is reproducibly observed across PS from different vendors, with modest variation depending on particle morphology and surface oxidation (Extended Data Fig. 1b). Time tracking of the process shows a continuous increase in interfacial fluorescence (Fig. 1g), indicating a sustained reaction. A linear fit to the time-dependent APF fluorescence yields a lower-bound estimate of the interfacial $\bullet\text{OH}$ production rate on the order of $0.1\text{--}1\text{ nM min}^{-1}$ (Extended Data Fig. 1d). Upon prolonged incubation (approximately 16 h; Fig. 1h), substantial conversion of APF can be achieved in the bulk suspension. Taken together, methyl orange

degradation, ESR detection with DMPO, spatially resolved APF imaging, and substantial APF conversion provide convergent evidence for spontaneous and sustained $\bullet\text{OH}$ generation at the PS–water interface.

If the reactivity pertains to the PS–water interface, it should be tunable by adding surfactants such as Triton X-100 to perturb the interfaces¹⁵. Indeed, ROS generation proves highly sensitive to the adsorption of this non-ionic surfactant (Fig. 1f–i). Adding 0.1% Triton X-100 markedly reduces the local fluorescence of APF at the PS–water interface (Fig. 1f), suppresses its temporal growth (Fig. 1g) and largely prevents APF conversion during prolonged incubation (Fig. 1h). More quantitatively, a pronounced dependence on Triton X-100 concentration is observed (Fig. 1i). As Triton X-100 itself does not inhibit the reaction between APF sensors and $\bullet\text{OH}$ (Extended Data Fig. 1c), the observed suppression of ROS generation is instead attributed to surfactant-induced modification of the PS–water interface.

Electrostatics at plastics–water interface

Polymer–water interfaces are often reported to acquire electric charges spontaneously^{34–36}, hence creating an electrostatically active environment that may contribute to the unusual reactivity at the water interface^{16,17,23}. To investigate this effect at microplastic–water interfaces, we perform electrophoresis measurements at the pristine surface of PS microplastics in water. X-ray photoelectron spectroscopy confirms the surface purity (vendor 1, Extended Data Fig. 1b). PS microplastics show a large negative zeta potential in pure water and 1 mM NaCl solution, which suggests the accumulation of negative charges at interfaces (Fig. 1j,k). As the surface potential gradient arises from the electrical double layer of charged species as described by Gouy–Chapman theory, we next use a positively charged dye Rhodamine 800 (Rh800) as a reporter of this environment. Confocal fluorescence microscopy reveals evident enrichment of Rh800 at the PS surface, confirming the electrophoresis measurement and corroborating the presence of an electrical double layer (Fig. 1l,m).

The physical surface electrostatics closely track its chemical reactivity. At the PS–ethanol interface, where no evident methyl orange degradation is observed (Fig. 1c), the zeta potential is much less negative and Rh800 shows minimal surface partitioning (Fig. 1k–m), underscoring the crucial role of water in activating PS surfaces with negative charges. Surface electrostatics can likewise be modulated with nonionic surfactants. In the presence of 0.1% Triton X-100, ROS generation is markedly reduced (Fig. 1f–i), the zeta potential of PS microplastics approaches zero (less than -5 mV ; Fig. 1j) and Rh800 shows negligible surface partitioning (Fig. 1l,m). Quantitatively, the physical and chemical activities of the PS–water interface show a strong inverse correlation across the four Triton X-100 conditions (Pearson correlation $r = -0.99$; Fig. 1j). It is noted that water-induced electrification differs fundamentally from surface charging by ionizable functional groups^{23,34}. For example, surface electrostatics arising from surface carboxyl groups cannot be modulated in the same way by solvent identity and non-ionic surfactant (Extended Data Fig. 2). Hence, water-induced surface electrostatics together with its tightly coupled radical generation constitute a novel effect for the intrinsic physicochemical activity of microplastic–water interfaces.

Chemical activity at aqueous microplastics surface

We next apply the same APF imaging assay across a panel of common commodity plastics, including PP, PE, PVC, PS, PET and PMMA. We observe spontaneous radical generation for all six types of microplastic (Fig. 2a), indicating that this chemical activity is a general feature of aqueous microplastic surfaces rather than a phenomenon unique to PS. Interestingly, the interfacial activities vary substantially among different plastic–water interfaces (Fig. 2b). Polyolefins, such as PE and PP, exhibit stronger activity compared with polymers containing

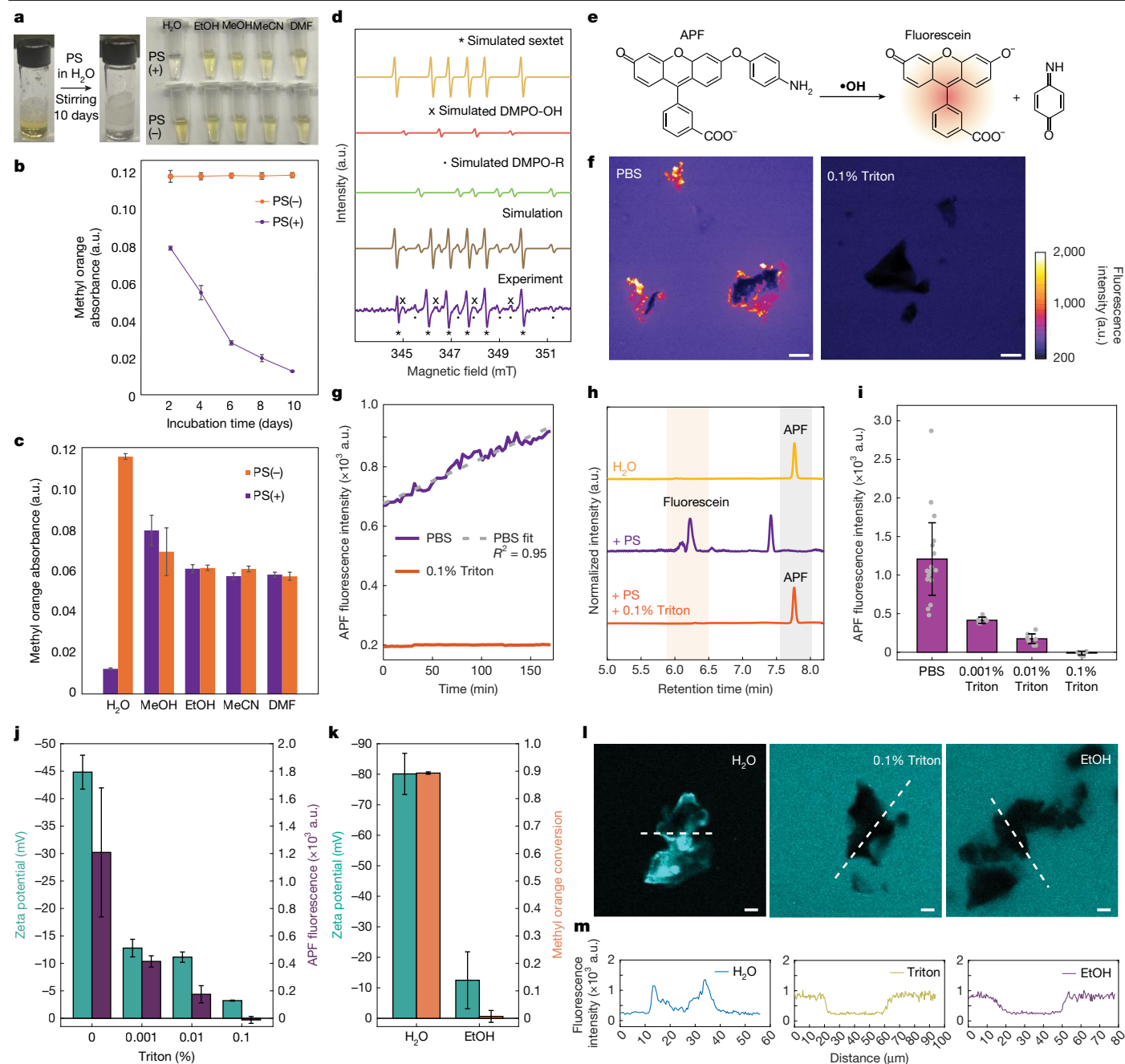


Fig. 1 | Spontaneous radical generation and surface electrostatics at PS microplastic–water interfaces. **a–i**, Spontaneous radical generation at PS microplastic–water interfaces. **a**, Left: photos showing methyl orange degradation in water after incubating with PS microplastics for 10 days. Right: supernatants collected from methyl orange solutions prepared in different solvents with (PS(+)) or without (PS(-)) PS microplastics after 10 days. **b**, Time trace of absorbance changes of methyl orange in water incubated with or without PS microplastics. Data are the mean $\pm$ s.d.; $n = 3$ aliquot measurements. Two-way repeated-measures analysis of variance; curves differed significantly ($P < 0.0001$). **c**, Methyl orange absorbance in solvents with or without PS microplastics after 10 days. Data are the mean $\pm$ s.d.; $n = 3$ aliquot measurements. **d**, ESR spectra of radicals generated by PS microplastics suspended in water using DMPO as a radical trapper; simulated and experimental spectra agree. Data are representative of three independent experiments. **e**, Reaction scheme of APF for $\bullet$ OH detection. **f**, Confocal fluorescence images of PS microplastics incubated with 5 μ M APF in PBS (left) or PBS containing 0.1% Triton X-100 (right). **g**, Time trace of APF fluorescence at a representative PS microparticle surface in PBS with or without Triton X-100. Data are representative of duplicate experiments. **h**, High-performance liquid chromatography analysis monitored at 488 nm confirms continuous APF conversion to fluorescein by PS microplastics in water,

whereas APF is fully retained when 0.1% Triton X-100 is present in the PS–water mixture. Data are representative of duplicate experiments. **i**, APF fluorescence quantification of PS microparticle surfaces in PBS containing varying Triton X-100 concentrations. Values are presented as area-weighted mean fluorescence intensities $\pm$ s.d. from particle regions at 0% ($n = 17$), 0.001% ($n = 6$), 0.01% ($n = 7$), and 0.1% ($n = 7$) Triton X-100, respectively. One-way analysis of variance with Tukey's test; PS in PBS differed from all Triton X-100 conditions ($P < 0.005$). **j–m**, Surface electrostatics at microplastics–water interfaces. **j**, Zeta potential of PS microplastics in 1 mM NaCl containing varying Triton X-100 concentrations (left axis) and their corresponding APF fluorescence at particle surfaces in PBS (right axis). Data are presented as mean $\pm$ s.d. Zeta potential data represent $n = 4$, 7, 5 and 4 independent measurements at 0%, 0.001%, 0.01%, and 0.1% Triton X-100, respectively. For the fluorescence measurement, the same data from panel i are shown here. **k**, Zeta potential of PS microplastics in water or ethanol (left axis) and corresponding methyl orange conversion (right axis). Data are mean $\pm$ s.d. Zeta potential data represent $n = 10$ and 3 independent measurements in water and ethanol, respectively. Methyl orange conversion is determined from $n = 3$ aliquot measurements. **l**, Surface electrostatics visualized using positively charged Rh800 (1 μ M) in water, 0.1% Triton X-100, or ethanol. **m**, Corresponding intensity profiles along the white dashed lines in panel l. Scale bars, 50 μ m (f), 20 μ m (l).

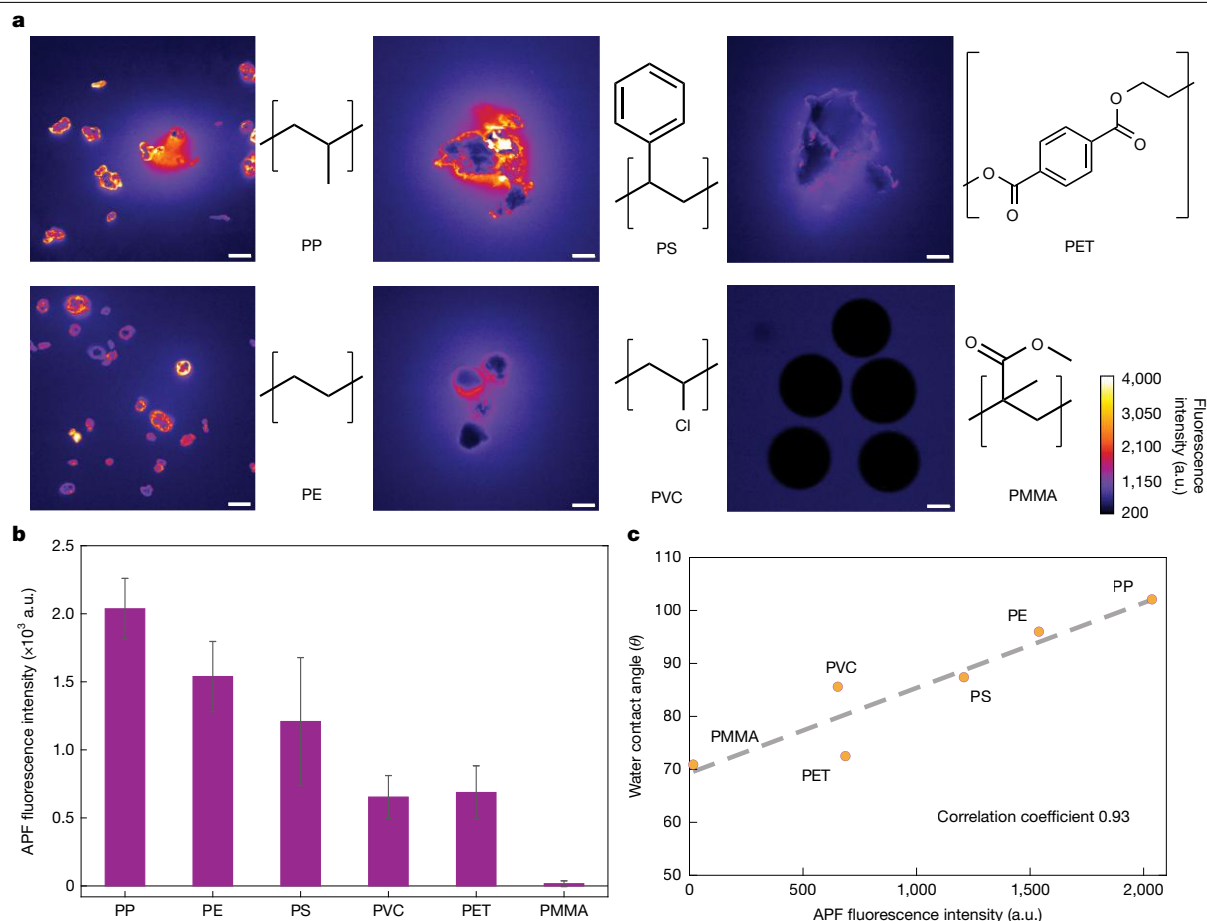


Fig. 2 | General chemical activity at microparticle–water interfaces across commodity plastics. **a**, Confocal fluorescence images of microplastics with different polymer compositions incubated with 5 μ M APF in PBS, with each corresponding chemical structure illustrated to the right. **b**, Quantification of APF fluorescence intensity measured at particle surfaces for different commodity plastics in PBS buffer. The background is subtracted from the fluorescence intensity of the same APF solution without adding microplastics.

Values are presented as area-weighted mean fluorescence intensities $\pm$ s.d from particle regions for PP ($n=10$), PE ($n=7$), PS ($n=17$), PVC ($n=10$), PET ($n=6$), and PMMA ($n=9$), respectively. **c**, Correlation between the water contact angle (θ) reported from the Accu Dyne Test Surface Energy Database³⁷ and APF fluorescence intensity measured at microplastic particle surfaces (same data from panel b) for different commodity plastics. Scale bars, 50 μ m (**a**).

additional hydrophilic functional groups, such as PET and PMMA. This trend suggests a connection with polymer hydrophobicity. Quantitatively, hydrophobicity at the solid–water interface is empirically measured by the water contact angle (θ), with larger θ corresponding to greater hydrophobicity³⁵. Therefore, we examine the correlation between interfacial activity measured by APF intensity and θ of the corresponding polymer from the reported database³⁷ (Fig. 2c), and identify a strong correlation (Pearson correlation $r=0.93$). Polyolefins with high hydrophobicity ($\theta > 90^\circ$) consistently correspond to the highest interfacial activity, whereas PMMA with lowest interfacial activity has highest hydrophilicity (with smallest θ).

Lower vertical ionization energies

We use molecular dynamics simulations and high-level ab initio calculations to understand the molecular underpinning of the radical generation trend with different plastic–water interfaces (Fig. 1) and its correlation with hydrophobicity (Fig. 2). We select three representative microplastics, PE, PVC and PMMA, for comparative studies and use vertical ionization energy (VIE) calculations to provide a quantitative metric of the propensity for $\bullet$ OH formation ($\text{OH}^- \rightarrow e^- + \bullet\text{OH}$) from OH^- (ref. 18) in solution with microplastics.

The VIE results for the PE–, PVC– and PMMA–water interfaces are summarized in Fig. 3a. All three systems show a dominant VIE peak at

approximately 210 kcal mol^{−1}, in excellent agreement with the experimental value (207 kcal mol^{−1}) for OH^- in bulk water³⁸. However, both the PE–water and PVC–water systems contain OH^- configurations with VIE values below 130 kcal mol^{−1}, with the more hydrophobic PE interface showing a larger low-VIE population. This trend is consistent with the reduced ionization energy in microdroplet chemistry²¹. OH^- is known to have water coordination numbers of about 4.0–6.0 in the bulk³⁹, whereas we find that the low-VIE tail for PE– and PVC–water arises predominantly from undercoordinated OH^- configurations (that is, partial solvation²²) located within approximately 5 Å of the Willard–Chandler interface (WCI)⁴⁰. As seen in Fig. 3b, these configurations are associated with partial solvation and characterized by hydrogen bonding between OH^- and the neighbouring water molecule bearing a dangling OH group (Fig. 3a, inset).

Undercoordinated water networks at the interface also help explain the variation in chemical activities among different plastics and their correlation with surface hydrophobicity (Fig. 3d). Compared with polyolefins, the somewhat less reactive PS contains phenyl rings that can act as weak hydrogen-bond acceptors through π -interaction, reducing the surface water dangling OH ratio to 21.0%; the electronegative chlorine atoms on PVC can likewise participate in weak hydrogen bonding, further reducing the dangling OH ratio to 15.8%; PMMA and PET, both containing hydrophilic ester moieties that are stronger hydrogen-bond acceptors, are most effective at suppressing interfacial dangling OH

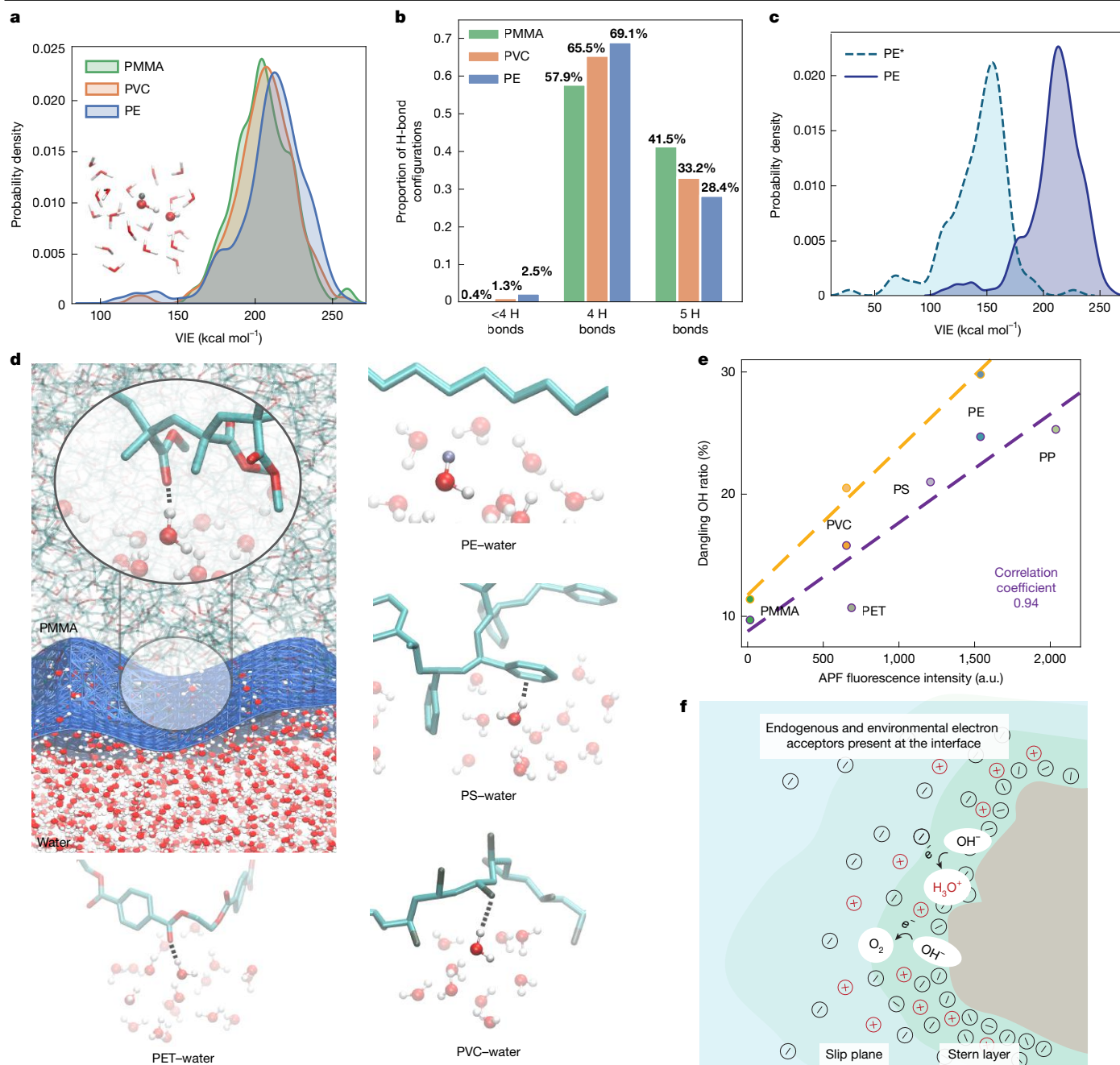


Fig. 3 | Theoretical investigations of the molecular structure–activity relationship at plastic–water interfaces. a, VIE distributions for OH⁻ obtained from 171, 153 and 184 configurations with converged electronic structure calculations for the PE, PVC and PMMA–water systems, respectively, each including explicit solvent molecules within 6 Å of the ion. The PE and PVC systems exhibit a distinct low-VIE tail (<130 kcal mol⁻¹), which predominantly arises from undercoordinated OH⁻ configurations at the interface. Inset: a representative snapshot sampled from the low-VIE tail region for water–PE interfaces, involving a direct hydrogen bond to a water with a surface dangling O–H bond (grey). **b**, Probability distribution of OH⁻ hydrogen-bond coordination within approximately 5 Å of the Willard–Chandler interface (WCI). Compared with PMMA, OH⁻ at the PE–water interface shows a much higher fraction of undercoordinated states (<4 hydrogen bonds), whereas PVC exhibits intermediate behaviour between the two systems. **c**, Comparison of VIE distributions of OH⁻ at the PE–water interface owing to stronger electric fields. The PE* with a dashed line represents the VIE distribution after removing

Na⁺ counterions from the PE–water system owing to a surface charge imbalance at the slip plane derived from the zeta potential. **d**, Hydrogen bonding to water across the hydrophobic to hydrophilic polymers; details of structural simulations are given in Supplementary Information. **e**, Simulated ratio of surface water dangling OH groups (defined as water without any acceptor (X) within an intermolecular O...X distance less than 3.5 Å and with an H–O...X angle (β) smaller than 50°) versus chemical activity indicated by APF fluorescence intensity measured at microplastic particle surfaces in Fig. 2b. Both OPLS-AA/SPC/E (purple line) and OPLS-AA/ReaxFF-C-GeM (yellow line) are shown. **f**, Electrical double-layer structure and potential electron acceptors and sinks at hydrophobic plastic–water interfaces. For example, O₂ and H⁺ may accept electrons from interface through the reactions OH⁻ + O₂ → •OH + •O₂⁻ and OH⁻ + H⁺ → •OH + •H, respectively. See Methods and Supplementary Information for details of the polymer and water models, molecular dynamics simulations, configuration sampling, structural analysis and VIE calculations.

populations (9.7% and 10.7%, respectively). Across the six polymer–water systems, the fraction of water dangling OH groups strongly correlates with the APF fluorescence (Pearson correlation $r = 0.94$; OPLS-AA/SPC/E; Fig. 3e), reduced tetrahedral order (Extended Data Fig. 5) and the empirical value of water contact angle (θ) (Extended Data Fig. 4a). Hence, a more hydrophobic interface corresponds to a higher degree of partial solvation and a more enhanced reactivity.

Hydrophobic water interfaces are often associated with the accumulation of negative charges and the resulting interfacial electric fields^{16,17}. Consistent with this, more hydrophobic PS and PE exhibit a more negative zeta potential than hydrophilic PMMA⁴¹ (Fig. 1 and Extended Data Fig. 4b). Hence, we remove Na^+ counterions to model the enhanced PE–water surface electrostatics, reflecting the net negative charge within the interfacial region inferred by the measured zeta potential at the slip plane. The resulting surface charge density, about 1 negative OH^- charge per 3 nm^2 , is comparable to the experimentally determined values for both oil nanodroplets and solid nanoparticles suspended in water^{42,43}. As shown in Fig. 3c, this additional electrostatic effect further shifts the VIE distribution towards energies well below $100 \text{ kcal mol}^{-1}$. This pronounced reduction in VIE lends strong support to the observed spontaneous radical generation (Figs. 1 and 2) and is also consistent with recent mechanistic studies of microdroplet chemistry^{16,17,19–21,26,27}.

Together, a higher population of undercoordinated OH^- (that is, partial solvation) and a more negatively charged water environment (electrostatic effect) would synergistically lower the VIE substantially to produce higher surface reactivity. This cooperative mechanism explains the correlated physical and chemical activities at PS–water interfaces across different Triton X-100 concentrations (Extended Data Fig. 6): adsorption of Triton X-100 at the interface suppresses water restructuring, reduces dangling OH groups and undercoordinated OH^- , and attenuates surface charging, collectively diminishing reactivity. Thermodynamically driven ion transfer at the polymer–water interface has been invoked to explain how a nominally uncharged polymer surface can acquire interfacial charge⁴⁴. The resulting negative zeta potentials may arise from an interfacial double layer analogous to that established at oil–water emulsions (Fig. 3f). Our calculations focus on the low-VIE states associated with undercoordinated OH^- at the most hydrophobic interface. Although complete electron removal remains energetically costly (approximately $100 \text{ kcal mol}^{-1}$), nearby electron acceptors such as hydronium or dissolved oxygen could provide coupled redox pathways, yielding $\cdot\text{H}$ (and ultimately H_2) or superoxide, respectively, and thereby compensate for the thermodynamic cost^{19,26,45,46}.

Biological implications to biomolecules and cells

Next we considered whether the intrinsic physicochemical activity at the surface of microplastics could influence their interactions with biomolecules and cells (Fig. 4a). Fluorescence imaging reveals that charged biomolecules gather at the microplastic–water interface (Fig. 4b). Positively charged wheat germ agglutinin (WGA), negatively charged R-phycoerythrin (R-PE), and DNA oligomers all partition to microplastic surfaces (Extended Data Fig. 3a). WGA exhibits greater interfacial enrichment than R-PE, consistent with the negative zeta potential of the microplastic surface (Extended Data Fig. 3b,c). Notably, biomolecular partitioning also tracks the hydrophobicity of microplastic–water interfaces: more hydrophobic PP microplastics show greater biomolecular enrichment than PMMA (Fig. 4b), and surfactant adsorption also modulates the surface enrichment accordingly (Fig. 4b). Thus, microplastic–water interfacial electrostatics contribute to the interaction between microplastics and charged biomolecules and may thereby regulate the surface corona formation⁴⁷.

Biomolecules attracted to the microplastic–water interface may also be subject to structural perturbations and even damage. To probe the possible structural changes of proteins, we use thioflavin T (ThT),

a fluorogenic probe for fibril formation and protein aggregation (Fig. 4c–g). Upon incubation of PS microplastics with ThT-stained lysozyme in phosphate-buffered saline (PBS), we find a gradual increase in the fluorescence signal at the PS–water interface (Fig. 4f), consistent with the formation of protein aggregates. To test whether the protein aggregation is driven by interfacial radical generation, we introduce caffeine, a well-established radical scavenger⁴⁸. Protein aggregation at the interface is significantly suppressed in the presence of caffeine, supporting a major role for surface-generated radicals in this structural damage (Fig. 4d). Likewise, coating PS surfaces with Triton X-100 prevents the protein structural disruption (Fig. 4e,f). Among different microplastic types, the tendency to induce protein aggregation resembles their interfacial physicochemical activity (Fig. 4g and Extended Data Fig. 3d; Pearson correlation $r = 0.68$), with polyolefins again exhibiting stronger effects than PET and PMMA.

How microplastics interact with cells can also be impacted. Using mouse red blood cells as a model, we assess the haemolytic activity following exposure to different microplastic particles. Haemolysis, which refers to the destruction of red blood cells, has been identified as one of the toxicological consequences of microplastic exposure⁴⁹. After incubation with PS microplastics in PBS, some initially disc-shaped mice red blood cells develop fragmented, helmet-like schistocyte morphologies following direct encounters with PS particles (Fig. 4h). Quantification of the released haemoglobin from red blood cells shows varying haemolytic activities, and this variation again correlates with the measured interfacial activity (Pearson correlation $r = 0.75$) for different commodity microplastics (Fig. 4i). Together, these findings show that microplastic–water interfaces can shape biomolecular adsorption, promote radical-associated protein damage and influence cellular injury.

Discussion

The global crisis of plastic pollution is compounded by the pervasive presence of microplastics. However, the fundamental question of how seemingly benign and chemically inert plastics become harmful when present as microplastics remains unresolved². Here we identify a previously overlooked property of microplastic–water interfaces: interfacial water can enable spontaneous $\cdot\text{OH}$ generation under ambient conditions. This mechanism is distinct from pathways driven by photoirradiation or chemical oxidation frequently associated with microplastic degradation in natural environments⁵⁰. Instead, this activity arises intrinsically from water–hydrophobe interactions and persists beyond pristine microplastics and simple buffer conditions (Extended Data Fig. 1b,d,e), although its magnitude can be modulated by surface morphology, functionalization and environmental context. This broadly relevant reactivity may therefore contribute not only to biomolecular and cellular damage at physiologically relevant rates but also to plastic ageing, co-pollutant transformation^{51,52} and even catalyst-free plastic upcycling⁵³.

Our work also provides insight into the fundamental chemistry of interfacial water. Hydrophobic water interfaces are known to exhibit distinctive structural, electrostatic and solvation properties^{15–17,19,23,34}, and these features have been implicated in the emerging field of microdroplet chemistry by reshaping reaction landscapes and promoting radical generation^{11–13,16,19,22,24,25,27–30}. Microplastic–water interfaces offer a tractable solid-supported platform for interrogating these effects systematically while connecting to environmental and public health consequences. Simulations quantify the energetic cost of $\cdot\text{OH}$ generation and reveal that interfacial water restructuring, partial solvation and surface electrostatics act synergistically to govern reactivity, providing a framework for further theoretical investigation. Moreover, this structure–activity relationship suggests an engineering principle: surface–water interactions should be considered as an additional design variable to meet the growing demand of safer and more sustainable materials.

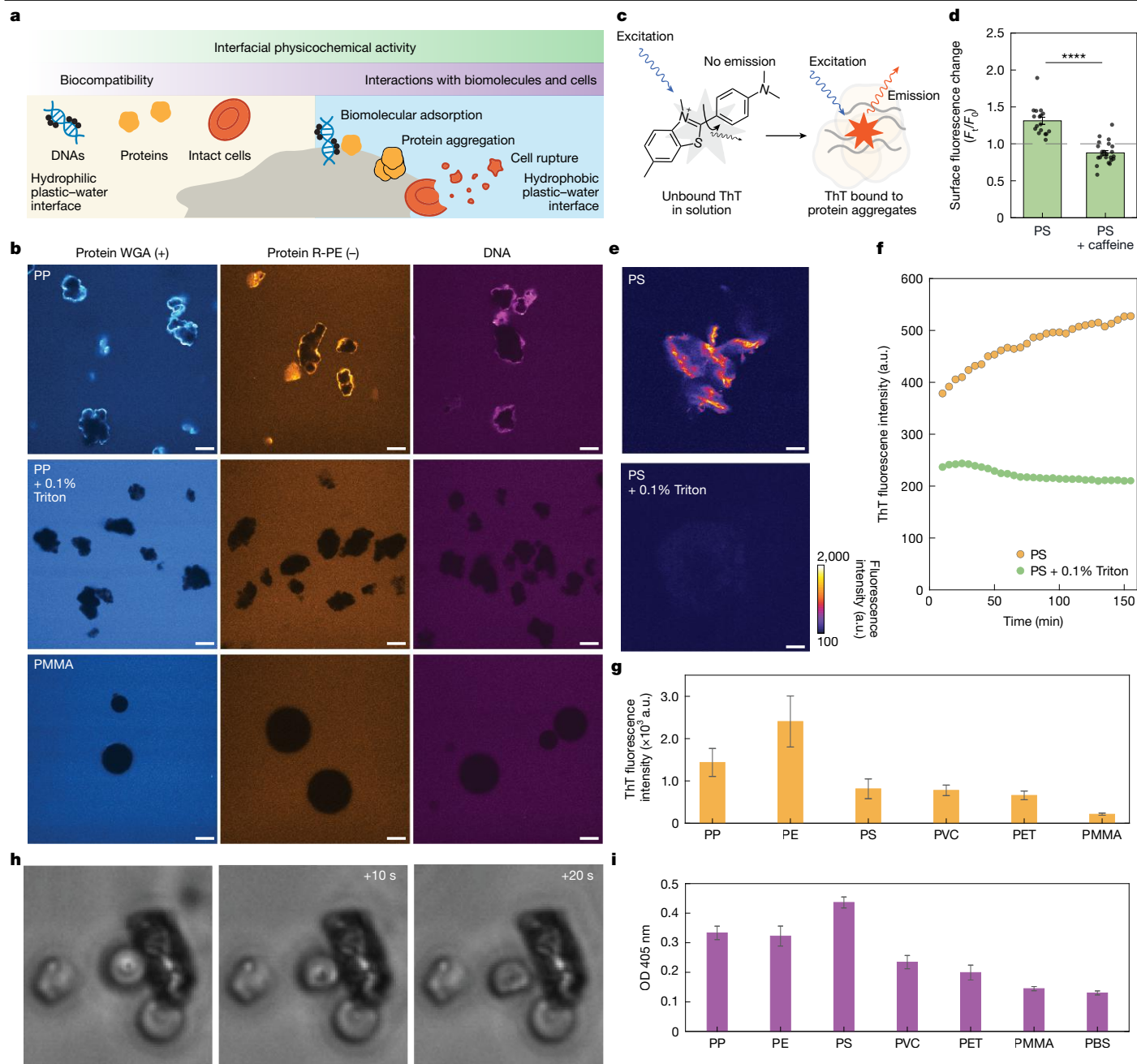


Fig. 4 | Biomolecular and cellular interactions regulated by plastics–water interfaces. **a**, An illustration of accumulation and damage of biomolecules and cells at microplastic surfaces. **b**, Confocal fluorescence imaging of charged biomolecules, including positively charged proteins such as WGA (left), negatively charged R-PE (middle), and DNA (right), revealed their selective partitioning at the plastic–water interface. Strong accumulation of charged biomolecules is observed on PP microplastics, whereas negligible accumulation is observed on more hydrophilic PMMA or the same PP with 0.1% Triton X-100. **c–g**, Protein aggregation arising from intrinsic physicochemical activity at plastic–water interfaces. **c**, An illustration of fluorogenic ThT assay for imaging protein aggregation. **d**, Thioflavin surface fluorescence (F_t/F_0 , where F_0 and F_t denote the surface fluorescence of the same particle before and after incubation) for lysozyme on PS microplastics with and without caffeine (a radical scavenger). The reference line ($F_t/F_0 = 1$) is indicated by the grey dashed line. Caffeine can completely suppress protein aggregation, as reflected by most data points at or below the reference line. Points indicate fluorescence from individual particles; $n = 17$ and 23 individual particles for PS and PS with caffeine, respectively. Data are mean $\pm$ s.e.m. **** $P < 0.0001$ (two-sided Wilcoxon rank-sum test). **e**, Confocal images of ThT binding to protein aggregates from lysozyme at PS–water interfaces in PBS buffer or in the presence of 0.1% Triton X-100 after equal incubation time. **f**, Time trace of ThT fluorescence intensity at PS–water interfaces, with or without Triton X-100. Data are representative of duplicate experiments. **g**, ThT fluorescence intensity quantification measured at particle surfaces of different commodity plastics with 0.1 mg ml^{−1} lysozyme in PBS buffer. Values are presented as area-weighted mean fluorescence intensities $\pm$ s.d. from particle regions for PP ($n = 10$), PE ($n = 10$), PS ($n = 7$), PVC ($n = 7$), PET ($n = 6$), and PMMA ($n = 6$), respectively. **h–i**, Microplastic interactions with cells as demonstrated by haemolytic activity. **h**, Erythrocytes fragmented into schistocytes upon interaction with PS microplastics as shown by the time-lapse optical micrographs. **i**, Haemolytic activity quantification for different commodity microplastics by measuring the optical density (OD; absorbance) at 405 nm of haemoglobin released into the supernatant. PBS buffer with no microplastic is utilized as a control. Data are mean $\pm$ s.d.; $n = 4$ independently prepared samples per group, including the PBS control. Scale bars, 50 μ m (**b**, **e**).

More broadly, the discovery of intrinsic physicochemical activity from water–microplastic interfaces has broad implications spanning environmental science, human health, materials engineering and the fundamental science of water.

Online content

Any methods, additional references, NaturePortfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-026-11141-y>.

- Thompson, R. C. et al. Twenty years of microplastic pollution research—what have we learned? *Science* **386**, eadl2746 (2024).
- Lamoree, M. H. et al. Health impacts of microplastic and nanoplastic exposure. *Nat. Med.* **31**, 2873–2887 (2025).
- Marfella, R. et al. Microplastics and nanoplastics in atheromas and cardiovascular events. *N. Engl. J. Med.* **390**, 900–910 (2024).
- Das, A. The emerging role of microplastics in systemic toxicity: Involvement of reactive oxygen species (ROS). *Sci. Total Environ.* **895**, 165076 (2023).
- Nihart, A. J. et al. Bioaccumulation of microplastics in decedent human brains. *Nat. Med.* **31**, 1114–1119 (2025).
- Liu, Z. & You, X. Recent progress of microplastic toxicity on human exposure base on in vitro and in vivo studies. *Sci. Total Environ.* **903**, 166766 (2023).
- Amerah, F. et al. Placental plastics in young women from general population correlate with reduced foetal growth in IUGR pregnancies. *Environ. Pollut.* **314**, 120174 (2022).
- Yan, Z. et al. Analysis of microplastics in human feces reveals a correlation between fecal microplastics and inflammatory bowel disease status. *Environ. Sci. Technol.* **56**, 414–421 (2022).
- Zhao, J., Zhang, H., Shi, L., Jia, Y. & Sheng, H. Detection and quantification of microplastics in various types of human tumor tissues. *Ecotoxicol. Environ. Saf.* **283**, 116818 (2024).
- Li, Y. et al. Potential health impact of microplastics: a review of environmental distribution, human exposure, and toxic effects. *Environ. Health* **1**, 249–257 (2023).
- Jin, S. et al. The spontaneous electron-mediated redox processes on sprayed water microdroplets. *JACS Au* **3**, 1563–1571 (2023).
- Ruiz-Lopez, M. F., Francisco, J. S., Martins-Costa, M. T. C. & Anglada, J. M. Molecular reactions at aqueous interfaces. *Nat. Rev. Chem.* **4**, 459–475 (2020).
- Li, K. et al. Spontaneous dark formation of OH radicals at the interface of aqueous atmospheric droplets. *Proc. Natl Acad. Sci. USA* **120**, e2220228120 (2023).
- Lee, K. et al. Catalyst-free selective oxidation of C(sp³)–H bonds in toluene on water. *Nat. Commun.* **15**, 6127 (2024).
- Shi, L. et al. Water structure and electric fields at the interface of oil droplets. *Nature* **640**, 87–93 (2025).
- LaCour, R. A., Heindel, J. P., Zhao, R. & Head-Gordon, T. The role of interfaces and charge for chemical reactivity in microdroplets. *J. Am. Chem. Soc.* **147**, 6299–6317 (2025).
- Chan, K. Y. et al. Electric fields at hydrophobic water interfaces: spectroscopic evidence, physical origin, and implications on reactivity. *Chem. Soc. Rev.* <https://doi.org/10.1039/D5CS00778J> (2025).
- Heindel, J. P., Hao, H., LaCour, R. A. & Head-Gordon, T. Spontaneous formation of hydrogen peroxide in water microdroplets. *J. Phys. Chem. Lett.* **13**, 10035–10041 (2022).
- Heindel, J. P., LaCour, R. A. & Head-Gordon, T. The role of charge in microdroplet redox chemistry. *Nat. Commun.* **15**, 3670 (2024).
- Hao, H., Leven, I. & Head-Gordon, T. Can electric fields drive chemistry for an aqueous microdroplet? *Nat. Commun.* **13**, 280 (2022).
- Holden, D. T., Shira, B. A., Edwards, M. Q., Morato, N. M. & Cooks, R. G. Mechanisms of ionization and of chemical reactions in charged microdroplets. *Chem. Sci.* **16**, 17020–17033 (2025).
- Cooks, R. G. & Pradeep, T. Accelerated chemistry in microdroplets. *Acc. Chem. Res.* <https://doi.org/10.1021/acs.accounts.6c00099> (2026).
- Li, S., Wang, Z. L. & Wei, D. Chemical reactions at electrified interfaces. *Acc. Chem. Res.* **59**, 285–297 (2026).
- Mehrgardi, M. A., Mofidfar, M. & Zare, R. N. Sprayed water microdroplets are able to generate hydrogen peroxide spontaneously. *J. Am. Chem. Soc.* **144**, 7606–7609 (2022).
- Lee, J. K., Samanta, D., Nam, H. G. & Zare, R. N. Micrometer-sized water droplets induce spontaneous reduction. *J. Am. Chem. Soc.* **141**, 10585–10589 (2019).
- Zhuang, C., Qian, N. & Min, W. Quantum tunneling on water. I. General framework for microdroplet redox chemistry. *J. Chem. Phys.* **164**, 224709 (2026).
- Jia, X., Wu, J. & Wang, F. Water-microdroplet-driven interface-charged chemistries. *JACS Au* **4**, 4141–4147 (2024).
- Xing, D. et al. Capture of hydroxyl radicals by hydronium cations in water microdroplets. *Angew. Chem. Int. Ed.* **134**, e202207587 (2022).
- Zhang, X. et al. Detection and characterization of water radical cations by mass spectrometry and electron paramagnetic resonance spectroscopy. *Anal. Chem.* **97**, 16004–16010 (2025).
- Liu, Y. et al. Strong electric field force at the air/water interface drives fast sulfate production in the atmosphere. *Chem.* **10**, 330–351 (2024).
- Wang, Z. et al. Contact-electro-catalysis for the degradation of organic pollutants using pristine dielectric powders. *Nat. Commun.* **13**, 130 (2022).
- Li, L. et al. Electron paramagnetic resonance tracks condition-sensitive water radical cation. *J. Phys. Chem. Lett.* **14**, 9183–9191 (2023).
- Emmanuel, S. S., Adesibikan, A. A., Opatola, E. A. & Olawoyin, C. O. A pragmatic review on photocatalytic degradation of methyl orange dye pollutant using greenly biofunctionalized nanometallic materials: a focus on aquatic body. *Appl. Organomet. Chem.* **37**, e7108 (2023).
- McCarty, L. S. & Whitesides, G. M. Electrostatic charging due to separation of ions at interfaces: contact electrification of ionic electrets. *Angew. Chem. Int. Ed.* **47**, 2188–2207 (2008).
- Kuehn, N., Jacobasch, H.-J. & Lunkenheimer, K. Zum Zusammenhang zwischen dem Kontaktwinkel zwischen Wasser und festen Polymeren und ihrem Zeta-Potential gegenüber wäßrigen Lösungen. *Acta Polym.* **37**, 394–396 (1986).
- Nauruzbayeva, J. et al. Electrification at water–hydrophobe interfaces. *Nat. Commun.* **11**, 5285 (2020).
- Diversified Enterprises. Critical surface tension and contact angle with water for various polymers. https://www.accudynetest.com/polytable_03.html?sortBy=contact_angle (accessed 24 May 2025).
- Winter, B., Faubel, M., Vácha, R. & Jungwirth, P. Behavior of hydroxide at the water/vapor interface. *Chem. Phys. Lett.* **474**, 241–247 (2009).
- Tuckerman, M., Laasonen, K., Sprik, M. & Parrinello, M. Ab initio molecular dynamics simulation of the solvation and transport of hydronium and hydroxyl ions in water. *J. Chem. Phys.* **103**, 150–161 (1995).
- Willard, A. P. & Chandler, D. Instantaneous Liquid Interfaces. *J. Phys. Chem. B* **114**, 1954–1958 (2010).
- Falahati, H. et al. The zeta potential of PMMA in contact with electrolytes of various conditions: theoretical and experimental investigation. *Electrophoresis* **35**, 870–882 (2014).
- Beattie, J. K. & Djerdjev, A. M. The pristine oil/water interface: surfactant-free hydroxide-charged emulsions. *Angew. Chem. Int. Ed.* **43**, 3568–3571 (2004).
- Preocanin, T. et al. Surface charge at Teflon/aqueous solution of potassium chloride interfaces. *Colloids Surf. A* **412**, 120–128 (2012).
- Zhang, H., Sundaresan, S. & Webb, M. A. Thermodynamic driving forces in contact electrification between polymeric materials. *Nat. Commun.* **15**, 2616 (2024).
- Eatoo, M. A. & Mishra, H. Disentangling the roles of dissolved oxygen, common salts, and pH on spontaneous hydrogen peroxide production in water: no O₂, no H₂O₂. *J. Am. Chem. Soc.* **147**, 35392–35400 (2025).
- Colussi, A. J. Mechanism of hydrogen peroxide formation on sprayed water microdroplets. *J. Am. Chem. Soc.* **145**, 16315–16317 (2023).
- Luo, H., Du, Q., Zhong, Z., Xu, Y. & Peng, J. Protein-coated microplastics corona complex: an underestimated risk of microplastics. *Sci. Total Environ.* **851**, 157948 (2022).
- Shi, X., Dalal, N. S. & Jain, A. C. Antioxidant behaviour of caffeine: efficient scavenging of hydroxyl radicals. *Food Chem. Toxicol.* **29**, 1–6 (1991).
- Choi, D. et al. In vitro toxicity from a physical perspective of polyethylene microplastics based on statistical curvature change analysis. *Sci. Total Environ.* **752**, 142242 (2021).
- Zeng, G. et al. Hydroxyl radicals in natural waters: light/dark mechanisms, changes and scavenging effects. *Sci. Total Environ.* **868**, 161533 (2023).
- He, W. et al. Recent advances on microplastic aging: identification, mechanism, influence factors, and additives release. *Sci. Total Environ.* **889**, 164035 (2023).
- Wang, T. et al. Interactions between microplastics and organic pollutants: effects on toxicity, bioaccumulation, degradation, and transport. *Sci. Total Environ.* **748**, 142427 (2020).
- Gao, R. et al. Catalyst-free, microdroplet-mediated waste plastic conversion to diacids. *Nature* **655**, 917–924 (2026).

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Methods

Chemicals and materials

PS microplastic powder with pristine surfaces was purchased with analytical standard grade from Sigma-Aldrich. PS microplastics with different morphologies were purchased from Thermo Fisher and Chem-Impex. The surface purity of model PS microplastics was characterized by X-ray photoelectron spectroscopy (PHI Versaprobe II X-ray Photoelectron Spectroscopy) before subsequent experiments. PE, PMMA and PVC were obtained in the format of micrometre-sized powder from Sigma-Aldrich. PET and PP powder were purchased from Goodfellow and Magerials Science, respectively.

Rh800 was obtained from Sigma-Aldrich. DMPO was purchased from TCI America. Triton X-100, methyl orange and ThT were obtained from Thermo Fisher. APF (Thermo Fisher Scientific) was obtained as 5 mM stock in *N,N*-dimethylformamide (DMF) and freshly diluted with phosphate-buffered saline (PBS; pH 7.4) to working concentrations before imaging for robust fluorescence quantification under a microscope. R-PE (BioLegend) and WGA–Alexa Fluor 647 conjugate (Thermo Fisher Scientific) were used as model charged biomolecules to visualize distribution at plastic surface. Alexa 660-labelled single-stranded DNA (5'-Alexa 660-CAC GCG AAG ACT TAA GAT A-3') was synthesized and purified by Integrated DNA Technologies.

All aqueous solutions were prepared using Milli-Q ultrapure water (18.2 MΩ·cm). Solvents including methanol (MeOH), ethanol (EtOH), acetonitrile (MeCN) and DMF were of HPLC grade. Standard buffers and salts (NaCl, FeCl₂, NaOH, triethylammonium acetate and trifluoroacetic acid) were purchased from Sigma-Aldrich unless otherwise specified.

Microscopy consumables, including glass coverslips, were pre-cleaned by piranha solution (3:1 H₂SO₄:H₂O₂) followed by copious rinsing with water unless otherwise specified. Disposable cuvettes were used for zeta-potential measurements with a Malvern ZS Nanosizer instrument.

Methyl orange degradation

Methyl orange solution (20 μM) was prepared with different solvents (that is, H₂O, MeOH, EtOH, MeCN and DMF) and mixed with PS powder (Sigma-Aldrich) at 10 mg ml⁻¹ concentration. The obtained suspension or solution was kept stirring at room temperature at a stir rate of 900 rpm for 10 days. Aliquots were taken every 2 days to monitor the possible degradation of methyl orange. Suspensions were centrifuged at 16,000 rpm for 3 min to obtain the supernatant. Methyl orange absorbance was calculated as $OD_{465nm} - OD_{700nm}$, where OD_{465nm} and OD_{700nm} are the optical densities measured at 465 and 700 nm, respectively. Subtraction of OD_{700nm} corrected for background signal, including scattering from residual particles. Supernatants were measured in three technical replicate wells (100 μl per well) using a 96-well plate reader. Methyl orange solution prepared with the same solvents at the same concentration without PS addition were kept under the same conditions and monitored at the same time as controls.

ESR measurements

DMPO was utilized to trap the radicals for ESR spectroscopy detection. To analyse the spontaneous formation of radical species at the PS–water interface, 200 mg PS powder was mixed with 20 mM DMPO solution in water. The suspension was incubated at room temperature for 20 min before filtration to collect the filtrate. The resulting filtrate was transferred into a Wilmad Glass quartz flat cell for ESR spectroscopy measurements. The spectra were acquired at room temperature with a Bruker ELEXSYS E500 EPR spectrometer under the following conditions: microwave power 20.23 mW; 12 scans averaged; centre field 3,480 G; sweep width 100 G; modulation amplitude 1 G; microwave frequency 9.768037 GHz.

APF radical sensing assay

Confocal fluorescence imaging. APF (5 mM; Thermo Fisher) was diluted to 5 μM using PBS. Then 1 ml of 5 μM APF was mixed with approximately 1 mg of microplastic particles (PP, PS, PE, PET, PVC or PMMA) through vortexing. Aliquots of the mixture were sandwiched in a glass chamber made by an imaging spacer separating the piranha-solution-treated cover glass and glass slide. Confocal fluorescence imaging was performed immediately after sample preparation. The green fluorescence channel was excited with an argon laser at 488 nm and emission was collected within a 505–520 nm band. Time-lapse images were acquired every 3 min with the excitation power optimized to minimize photobleaching and other perturbations during in situ tracking of the fluorogenic APF signal.

For endpoint quantification of the APF assay, mixtures containing 5 μM APF and approximately 1 mg of microplastic particles (PP, PS, PE, PET, PVC or PMMA) were first dispersed by vortexing and then incubated in the dark at room temperature for 90 min to allow the fluorogenic reaction to progress at the plastic–water interface. After incubation, aliquots of each sample were mounted in imaging chambers composed of a poly-L-lysine coated coverslip (Neuvitro) and a glass slide separated by a spacer. Fluorescence images were acquired with constant laser power, photomultiplier tube (PMT) voltage, detector gain and pinhole size across all measurements to ensure quantitative comparability. Multiple non-overlapping fields of view were imaged for each polymer type to account for potential spatial heterogeneity in fluorescence signal distribution.

Quantification of APF fluorescence was performed after generating maximum-intensity Z projections from the acquired confocal stacks. Particle regions of interest were segmented using corresponding stimulated Raman scattering (SRS) images as references to accurately define particle boundaries. The fluorescence intensities were then extracted as area-weighted averages from the segmented regions of interest to represent the relative reactivity of each microplastic type.

SRS imaging. We used SRS imaging to characterize microplastics together with confocal imaging analysis⁵⁴. SRS imaging was conducted on a confocal laser-scanning microscope (FV1200, Olympus) integrated with customized laser sources. A commercial laser system (PicoEmerald S, Applied Physics & Electronics) provided both the pump and Stokes beams. The Stokes wavelength was fixed at 1,031.8 nm and modulated at 20 MHz by an electro-optic modulator, whereas the pump beam was tunable and set to 784.2 nm to excite C–H vibrational modes characteristic of microplastics. Both beams with an approximately 2-ps pulse width and 80-MHz repetition rate, were spatially and temporally synchronized, and tightly focused onto the sample using a ×25 water-immersion objective (XLPlan N, 1.05 NA MP, Olympus). The transmitted beams were collected by an oil-immersion condenser with a numerical aperture of 1.4, with the Stokes beam removed by a high-optical-density bandpass filter (890/220 CARS, Chroma Technology). The transmitted pump beam was detected by a silicon photodiode (S3590-09, Hamamatsu) under 64-V bias. The photodiode output was terminated through a 50-Ω load, and demodulated using a high-frequency lock-in amplifier (HF2LI, Zurich Instruments) at 20 MHz. The demodulated pump-loss signal was digitized and transmitted to the FV10 analogue input channel to generate SRS images.

HPLC analysis. An Agilent 1200 series system equipped with a Vydac 218TP-C18 column (250 × 4.6 mm, 5 μm; Grace) was utilized for HPLC analysis. The gradient was increased from 5% B to 95% B in 15 min (solvent A, water + 0.1 M triethylammonium acetate; solvent B, acetonitrile + 0.1% (v/v) trifluoroacetic acid). The detection unit was set to monitor the reaction by the absorbance at 488 nm. The peaks corresponding to APF and its oxidation product, fluorescein, were assigned based on the retention time measured from the standard solution.

To examine the APF conversion in water upon PS powder addition, 100 mg PS powder was suspended in 1 ml of 20 μ M APF solution in water with and without 0.1% Triton X-100 supplement. The suspension was left stirring in the dark for 16 h at room temperature before filtration to collect the filtrate for HPLC analysis. A positive control was prepared by mixing 20 μ M APF with 20 mM H_2O_2 and 2 mM FeCl_2 in water and incubated for the same duration before HPLC analysis.

Surface localization imaging assay

Surface localization of charged fluorophore. PS particles (1 mg ml^{-1}) were suspended in 1 μ M Rh800 prepared under different solvent conditions (that is, H_2O , 0.1% Triton X-100 in H_2O , and EtOH). The suspensions were incubated in the dark at room temperature for 10 min before confocal fluorescence imaging. The far-red channel was excited by an 635-nm laser with a collection band of 655–755 nm.

Surface localization of protein. Plastic particles (10 mg ml^{-1}) were mixed with protein in PBS (0.02 mg ml^{-1}) to image the surface of absorption of the protein under confocal fluorescence imaging. Proteins with different net charges in the PBS environment were selected with R-PE (Biolegend) being negatively charged and WGA (Thermo Fisher, W32466) being positively charged at pH 7.4. The mixture was vortexed and incubated in the dark for 15 min before an aliquot of the mixture was sandwiched in a glass chamber in the same way with piranha-solution-treated cover glass. WGA conjugated with Alexa Fluor 647 was imaged in the far-red channel, excited by an 635-nm laser with fluorescence collected between 655 nm and 755 nm. R-PE was imaged in the red channel, excited by a HeNe(G) laser (543 nm) with emission collected between 560 nm and 660 nm. Simultaneous imaging of the two channels revealed the different partition pattern of oppositely charged proteins on plastic surfaces.

Surface localization of DNA. Alexa 660-labelled DNA (500 nM; 5'-Alexa 660-CAC GCG AAG ACT TAA GAT A-3', from Integrated DNA Technologies) was added to plastic particles (approximately 10 mg ml^{-1}) to image the surface adsorption of the DNA molecules under confocal fluorescence imaging. The mixture was vortexed and incubated in the dark for 15 min before an aliquot of the mixture was sandwiched in a glass chamber in the same way with a piranha-solution-treated cover glass for confocal imaging with the far-red channel excited by an 635-nm laser, and emission was collected at 655–755 nm.

ThT assay for protein aggregation analysis. ThT is widely used as a 'gold standard' for selectively staining and identifying amyloid fibril formation both in vivo and in vitro⁵⁵. Here, 0.1 mg ml^{-1} lysozyme solution stained with 20 μ M ThT in PBS was mixed with plastic particles at a concentration of 1 mg ml^{-1} . The mixture was vortexed before an aliquot was sandwiched in a glass chamber in the same way with a piranha-solution-treated cover glass for confocal fluorescence imaging. ThT fluorescence was excited at 488 nm and collected in the 505–520 nm emission window. Time-lapse imaging was performed on selected particles at 5-min intervals.

Fluorescence images for quantification of the ThT assay for different microplastics were acquired after incubating the mixture in the dark for 2 h. z-stack images were acquired for each region of interest to map the thioflavin fluorescence at the particle surface. Quantification of the fluorescence signal are performed after z-stack projection (maximum intensity) by segmenting the particles in reference to the corresponding SRS images (method described in 'SRS imaging') and measured the area-weighted average fluorescence for segmented particle regions of interest.

For the experiment comparing the effect of radical scavenger on protein aggregation at the PS–water interface, ThT fluorescence was monitored using a BioTek Cytation 9 Cell Imaging Multimode Reader. Samples containing 4 mg ml^{-1} PS microplastics, 0.1 mg ml^{-1} lysozyme

and 20 μ M ThT in PBS, with or without 100 mM caffeine, were prepared in a 24-well plate and imaged as z-stacks with a $\times 20$ objective before and after a 4-h incubation at 37 °C in the dark inside the instrument. A 4% agarose gel pad prepared in PBS to minimize particle movement in solution during imaging. Five to six fields of view were defined for each condition and the same particle retained within each field at the two time points were identified and analysed. Surface-associated ThT fluorescence was quantified as the average fluorescence intensity over the particle area, and the fluorescence change for each particle was calculated as F_i/F_0 , where F_0 and F_i denote the surface fluorescence of the same particle before and after incubation, respectively.

Haemolytic assay. Mouse whole blood was collected from wild-type mice (BALB/cJ, 20 weeks old, Jackson Lab) with an animal protocol (AC-AABN0554) approved by the Institutional Animal Care and Use Committee (IACUC) at Columbia University. A final concentration of approximate 10 mM EDTA was supplemented to prevent coagulation. Haemolysis was assessed using a published protocol⁵⁶. As soon as possible after phlebotomy, the blood samples were centrifuged at 1,700 g for 5 min. The supernatant was removed by aspiration and 2 ml PBS pH 7 was added. The washing step was repeated three times or until the supernatant was clear. After final aspiration, the remaining pellet was diluted in PBS (1:100) to obtain erythrocyte suspension. To test haemolytic activity, 150 μ l of obtained erythrocyte suspension was gently mixed with 2 mg plastic particles and incubated for 60 min at 37 °C without agitation before centrifuged at 1,700g for 5 min to collect the supernatant. The same erythrocyte suspension with no plastic particles was examined as a negative control. Haemolytic activity was then quantified by measuring optical density at 405 nm ($\text{OD}_{405\text{nm}}$) of the supernatant using a plate reader with 96-well plates.

Zeta-potential measurement. The electrophoretic mobilities of PS particles in different conditions were measured using a Malvern ZS Nanosizer instrument. Pristine PS microparticles or carboxylic-acid-functionalized PS microparticles were prepared with a concentration of 1 mg ml^{-1} in 1 mM NaCl aqueous solution to examine the sensitivity of their surface electrostatics to different concentrations of Triton X-100 supplement. Pure water and ethanol were also used to suspend the pristine PS microparticles or carboxylic-acid-functionalized PS microparticles at the same concentration to compare their solvent sensitivity to the surface electrostatics. Zeta-potential (ζ) values were calculated from the electrophoretic mobility values using the following expression: $\mu = \frac{\varepsilon \varepsilon_0}{\eta} \zeta f(\kappa a)$, where ε_0 is the vacuum permittivity, ε is the relative permittivity of solvent, η is the viscosity of solvent and $f(\kappa a)$ is Henry's function. The Hückel formula was used to calculate the zeta potential and compare between different samples¹⁵. All measurements were performed at 25 °C with disposable plastic cuvettes.

Theory and simulation

Non-reactive and reactive force fields. For many of the structural analyses used in this study, we used the force-field combination of OPLS-AA for the polymer and the SPC/E water model. However, to generate configurations for the VIE calculations, we used a more sophisticated ReaxFF/C-GeM model to describe water, OH^- and Na^+ . Previous studies have shown that classical fixed-charge OH^- force fields often predict overcoordinated hydration environments, frequently yielding coordination numbers exceeding six. In contrast, ab initio simulations and experimental evidence indicate that hydroxide is best described as a hypercoordinated species with approximately three to five hydrogen bonds. In this context, reactive force-field approaches such as ReaxFF/C-GeM provide a more physical description by explicitly accounting for charge redistribution and proton-transfer dynamics. ReaxFF/C-GeM has been shown to accurately capture the energetics and dynamics of hydronium and hydroxide ion species⁵⁷. In particular, proton-transfer events that interconvert different

hydration states of hydroxide (for example, transitions between four- and three-hydrogen-bond configurations) have been identified as rate-controlling steps for hydroxide diffusion. ReaxFF/C-GeM has been shown to reproduce both the solvated structure of hydroxide and its diffusion coefficient in water with reasonable accuracy (for example, approximately $0.40 \text{ \AA}^2 \text{ ps}^{-1}$ from ReaxFF/C-GeM compared with approximately $0.56 \text{ \AA}^2 \text{ ps}^{-1}$ experimentally). Such capabilities are especially relevant for resolving interfacial hydration structure and ion mobility at polymer–water interfaces, which are central to the present study.

Electrostatic embedding model for ReaxFF/C-GeM. In this study, we performed MD simulations of an interfacial system of an aqueous NaOH solution with three microplastic systems in a slab geometry using an electrostatic embedding scheme by modelling the water and NaOH with the reactive force-field ReaxFF/C-GeM^{57,58}, and used the non-reactive OPLS-AA^{59,60} for PE, PVC and PMMA. The system is partitioned into three components:

1. ReaxFF/C-GeM atoms, which include all water and NaOH and are treated using the reactive force field.
2. All polymer atoms are described entirely by a non-reactive (OPLS-AA) force field.
3. Non-bonded interactions between the ReaxFF/C-GeM and OPLS-AA regions, including van der Waals and electrostatic interactions, which provide the coupling between the two force-field descriptions. For the van der Waals interactions, we adopt parameters consistent with the OPLS-AA/SPC/E force field, following the same protocol established in our previous work on reverse micelle systems⁶¹ and using the standard mixing rules of the OPLS force field. Water–polymer electrostatics are treated with fixed charges for the polymer and Gaussian charge density for the water and NaOH. See refs. 61,62 for further details.

Importantly, this electrostatic embedding modelling strategy has been used and validated in previous studies, including systems involving both neutral and charged reverse micelles^{61,62}. In those studies, the force-field combination was benchmarked against a range of experimental observables from dielectric relaxation and terahertz spectroscopy related to interfacial proton-transfer-related phenomena^{61,62}.

Further benchmarking of force-field combinations. We have also evaluated interaction energies and hydrogen-bond-related intermolecular distances for representative polymer–water model systems (Supplementary Table 1), constructed from small-molecule analogues and optimized consistently at each level of theory. As shown in Supplementary Table 1, both OPLS-AA/SPC/E and OPLS-AA/ReaxFF-C-GeM reproduce the correct qualitative trends in interaction strength across the different systems. Notably, the OPLS-AA/ReaxFF-C-GeM model shows improved agreement with density functional theory in both binding energies and intermolecular distances, particularly for PMMA, where stronger hydrogen-bonding interactions are more accurately captured. These results support that the hybrid OPLS-AA/ReaxFF-C-GeM approach provides a physically reasonable and reliable description of polymer–water interactions at the interface.

In addition, radial distribution functions between water and representative polymer surface atoms further confirm that both force-field descriptions yield consistent interfacial hydration structures, with only minor quantitative differences, as seen in Extended Data Fig. 7a–f. The two force-field descriptions (OPLS-AA/SPC/E and OPLS-AA/ReaxFF-C-GeM) yield overall consistent radial distribution function profiles across the three systems. For the PMMA system, the OPLS-AA/ReaxFF-C-GeM model exhibits a more pronounced first peak, indicating stronger water–polymer interactions. This is consistent with interaction energy analysis, which shows that hydrogen-bonding interactions are stronger in the OPLS-AA/ReaxFF-C-GeM description compared with OPLS-AA/SPC/E. Notably, this stronger interaction is in closer

agreement with density-functional-theory-level calculations, suggesting that the ReaxFF/C-GeM-based description provides a more accurate representation of interfacial hydrogen bonding in this system.

Simulation details for OPLS-AA/SPC/E used for structural analysis. For water–plastic interfaces, plastics and Triton X-100 surfactant molecules were modelled with the all-atom OPLS-AA force field^{59,60} and water using the SPC/E model. Each system consisted of a single long polymer chain in a slab geometry of approximately 40,000 polymer atoms and approximately 9,000 water molecules. Non-bonded interactions were truncated at 10 Å, and for SPC/E long-range electrostatics were computed using the particle–particle particle-mesh Ewald method with a convergence criterion of 10^{-5} . The molecular dynamics simulations were carried out using LAMMPS⁶³, and used a 1-fs timestep with SHAKE constraints applied to SPC/E water molecules⁶⁴. The temperature was maintained at 300 K using a Nosé–Hoover thermostat (damping constant 100 fs)⁶⁵, and constant pressure in the *z* direction (1 atm) was enforced.

The initial polymer slabs were prepared following the protocol previously described⁴⁴. The polymer systems were first equilibrated for 500 ps before introducing SPC/E water. After adding water above the slab, the system was further relaxed and equilibrated for 1 ns, followed by a 5-ns production run. Snapshots were saved every 10 ps, yielding 500 frames for structural analysis presented in Fig. 3d,e, and in Extended Data Figs. 4–6 and 7a–f.

Simulation details for OPLS-AA/ReaxFF-C-GeM used for structural analysis. We performed molecular dynamic simulations with the electrostatic embedded model using a modified version of LAMMPS for PE, PVC and PMMA⁵⁸. Each system consisted of a single long polymer chain in a slab geometry of approximately 8,000 polymer atoms and approximately 2,000 water molecules for ReaxFF/C-GeM. Non-bonded interactions were truncated at 10 Å. The simulations used a 0.25-fs timestep, the temperature was maintained at 300 K using a Nosé–Hoover thermostat (damping constant 100 fs)⁶⁵ and a constant pressure in the *z* direction (1 atm) was enforced. The initial polymer slabs were prepared following the protocol previously described⁴⁴. The polymer systems were first equilibrated for 500 ps before introducing water. After adding water above the slab, the system was further relaxed and equilibrated for 400 ps using ReaxFF/C-GeM, followed by a 2-ns production run. Snapshots were saved every 5 ps, yielding 400 frames for ReaxFF/C-GeM for structural analysis in Fig. 3e and in Extended Data Figs. 7 and 8.

Simulation quantities for the microplastics. To better characterize the polymer surfaces in our OPLS-AA simulations, we analysed both the polymer density and the distribution of exposed functional groups at the interface. Supplementary Table 2 shows that the equilibrated microplastic systems reproduce physically reasonable bulk densities using a standard 21-step protocol⁶⁶. We also computed the surface-exposed functional groups density profile, $\rho_{\text{poly}}(z)$, to identify the interfacial region. Within this region, surface-exposed functional groups were defined as those located within 4 Å of the Willard–Chandler interface (WCI, the instantaneous interface defined as the isodensity surface of the water oxygen density field at half of the bulk liquid density). We then evaluated the surface density of functional groups for each polymer system. As PE does not contain functional groups, it is not included in this analysis. For the other systems, we selected representative groups: chlorine atoms for PVC, the two oxygen atoms in the COOR group for PET and PMMA, and the aromatic ring centroid for PS. As shown in Extended Data Fig. 8a, the surface functional group densities exhibit narrow distributions, with relative fluctuations below approximately 5%, indicating that the exposed surface composition remains stable over the course of the simulation, without significant interfacial reconstruction. Furthermore, comparisons between OPLS-AA/SPC/E

and OPLS-AA/ReaxFF-C-GeM show only minor differences in the distributions, suggesting that the interfacial functional group exposure is robust with respect to the choice of water model. These results indicate that, although the polymer matrices are amorphous, the interfacial surface structure remains statistically stable on the simulation time-scale, supporting the reliability of the observed hydration and reactivity trends. Together, these results support the use of a single-chain representation for the present interfacial study.

VIE calculations and sampling details. For VIE calculations, 4 NaOH molecules were added to the water phase (box size approximately $3.6 \times 3.6 \times 7 \text{ nm}^3$) based on the surface charge density reported in ref. 42. VIEs were computed following the procedure in ref. 19 at the ω B97M-V level of theory using Q-Chem⁶⁷, with aug-cc-pVTZ for OH⁻/OH[•] and aug-cc-pVDZ for surrounding environments. Each calculation included explicit solvent within 6 Å of the hydroxide ion, with the remainder treated via charge embedding from atomic charges from the remaining simulated environment. Hydrogen bonds to OH⁻ were defined by a donor(water-H)–acceptor(O–H⁻) distance $\leq 2.7 \text{ Å}$ and an O–H–O angle $\geq 115^\circ$. All results are shown in Fig. 3a.

As the experimentally measured zeta potential reflects the potential at the slip plane, this implies a net charge imbalance within the interfacial region, that is, the particle effectively carries excess negative charge. To model this, we removed all Na⁺ ion as a practical way to reproduce this charge imbalance in a finite simulation set-up. Explicitly resolving the electrical double layer would require substantially larger system sizes and longer timescales than are currently feasible. Removing Na⁺ therefore provides a simple but direct way to impose an experimentally motivated interfacial charge density consistent with experimentally measured zeta potentials. All results are shown in Fig. 3c.

In our VIE calculations, configurations are constructed by including explicit solvent molecules within 6 Å of the hydroxide ion, which may exclude direct polymer–OH⁻ contacts in some interfacial configurations. To assess the impact of this approximation, we directly compared VIE values computed with and without configurations involving the OH⁻ proximity to the PE plastic. As shown in Extended Data Fig. 7g, the two sets of results are in close agreement on a per-configuration basis, with data points distributed near the parity line. The average VIE values are $192.99 \text{ kcal mol}^{-1}$ and $193.82 \text{ kcal mol}^{-1}$, differing by only $0.83 \text{ kcal mol}^{-1}$ ($<0.5\%$). These results indicate that excluding polymer atoms from the VIE region does not materially affect the computed ionization energies and that the VIE is primarily governed by the local solvation environment of hydroxide.

To ensure consistency and convergence across systems, all molecular dynamics simulations using ReaxFF/C-GeM are over a timescale of 2 ns for each polymer–water system. The time-resolved VIE distributions show that the statistics are well converged over the simulation time-scale, whereas the spatial distributions of undercoordinated hydroxide ions relative to the interface are consistent with the observed trends in VIE behaviour across different polymer systems. The results shown in the main text (Fig. 3a,c) were obtained from one representative 500-ps trajectory window, from which configurations were sampled every 2.5 ps. By contrast, Extended Data Fig. 8c–e is included primarily to demonstrate convergence across the full 2-ns simulation. For this analysis, the trajectory was divided into 4 consecutive 500-ps windows, and configurations were sampled every 5 ps within each window, yielding approximately 100 configurations per segment. Owing to occasional SCF convergence failures in the electronic-structure calculations, the number of successfully evaluated configurations is slightly reduced but remains sufficient to construct statistically meaningful VIE distributions. To improve the sampling of rare interfacial configurations, we additionally used a targeted sampling scheme based on structural criteria (distance to the WCI $<5 \text{ Å}$ and hydrogen-bond coordination number <4), with configurations selected at 1-ps intervals. As shown

in Extended Data Fig. 8c–e, the time-resolved VIE distributions reveal distinct behaviours across the three polymer systems. In the PE system, a low-VIE tail is observed in both the early and late trajectory segments, indicating that such configurations are sampled repeatedly over the course of the simulation. In the PVC system, a low-VIE tail emerges in the later trajectory segment (1.5–2.0 ns), consistent with the behaviour observed in PE, but with lower frequency, reflecting the presence of rare interfacial configurations. In contrast, as shown in Extended Data Fig. 8b, the PMMA system exhibits a substantially lower population of undercoordinated hydroxide ions in the interfacial region, and no configurations corresponding to the low-VIE tail are observed over the full 2-ns simulation. These observations further support the connection between interfacial hydroxide structure and VIE behaviour across different polymer systems.

Data availability

Source data are provided with this paper.

Code availability

The source code for LAMMPS is publicly available on GitHub at <https://github.com/lammps/lammps>. Electronic-structure calculations were performed using Q-Chem 6.0, which is available from Q-Chem, Inc. under a commercial license (<https://www.q-chem.com>). Analysis code for hydroxide hydrogen-bond coordination and interfacial water structure, together with an example set-up for running simulations using the hybrid ReaxFF–C-GeM/OPLS-AA force field, is available on GitHub at https://github.com/Ruo7Zhao/micropastic_water_interface.

54. Min, W., Cheng, J.-X. & Ozeki, Y. Theory, innovations and applications of stimulated Raman scattering microscopy. *Nat. Photon.* **19**, 803–816 (2025).
55. Biancalana, M. & Koide, S. Molecular mechanism of thioflavin-T binding to amyloid fibrils. *Biochim. Biophys. Acta Proteins Proteom.* **1804**, 1405–1412 (2010).
56. Sæbø, I., Bjørås, M., Franzyk, H., Helgesen, E. & Booth, J. Optimization of the hemolysis assay for the assessment of cytotoxicity. *Int. J. Mol. Sci.* **24**, 2914 (2023).
57. Leven, I., Hao, H., Das, A. K. & Head-Gordon, T. A reactive force field with coarse-grained electrons for liquid water. *J. Phys. Chem. Lett.* **11**, 9240–9247 (2020).
58. Leven, I. et al. Recent advances for improving the accuracy, transferability, and efficiency of reactive force fields. *J. Chem. Theory Comput.* **17**, 3237–3251 (2021).
59. Jorgensen, W. L., Maxwell, D. S. & Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.* **118**, 11225–11236 (1996).
60. Siu, S. W. I., Pluhackova, K. & Böckmann, R. A. Optimization of the OPLS-AA force field for long hydrocarbons. *J. Chem. Theory Comput.* **8**, 1459–1470 (2012).
61. Hao, H. et al. Highly altered state of proton transport in acid pools in charged reverse micelles. *J. Am. Chem. Soc.* **145**, 1826–1834 (2023).
62. Leven, I. & Head-Gordon, T. C-GeM: coarse-grained electron model for predicting the electrostatic potential in molecules. *J. Phys. Chem. Lett.* **10**, 6820–6826 (2019).
63. Thompson, A. P. et al. LAMMPS—a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.* **271**, 108171 (2022).
64. Ryckaert, J.-P., Cicciotti, G. & Berendsen, H. J. C. Numerical integration of the Cartesian equations of motion of a system with constraints: molecular dynamics of *n*-alkanes. *J. Comput. Phys.* **23**, 327–341 (1977).
65. Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* **31**, 1695–1697 (1985).
66. Abbott, L. J., Hart, K. E. & Colina, C. M. Polymatic: a generalized simulated polymerization algorithm for amorphous polymers. *Theor. Chem. Acc.* **132**, 1334 (2013).
67. Mardirossian, N. & Head-Gordon, M. ω B97M-V: a combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J. Chem. Phys.* **144**, 214110 (2016).
68. Setsukinai, K., Urano, Y., Kakinuma, K., Majima, H. J. & Nagano, T. Development of novel fluorescence probes that can reliably detect reactive oxygen species and distinguish specific species. *J. Biol. Chem.* **278**, 3170–3175 (2003).

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Author contributions N.Q. and W.M. conceived of the idea and designed the experiments. N.Q., K.Y.C. and V.G.V. performed the experiments. N.Q. and K.Y.C. analysed the experimental data. R.Z., R.A.L. and T.H.-G. formulated all the theoretical work and analysis. X.G., Z.Z., Y.D., P.A.S. and B.Y. contributed to critical reagents, protocols and analytical assays. N.Q., R.Z., T.H.-G. and W.M. wrote the paper. All authors contributed to discussion and revising text.

Article

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Competing interests Columbia University has filed a provisional patent application based on this work.

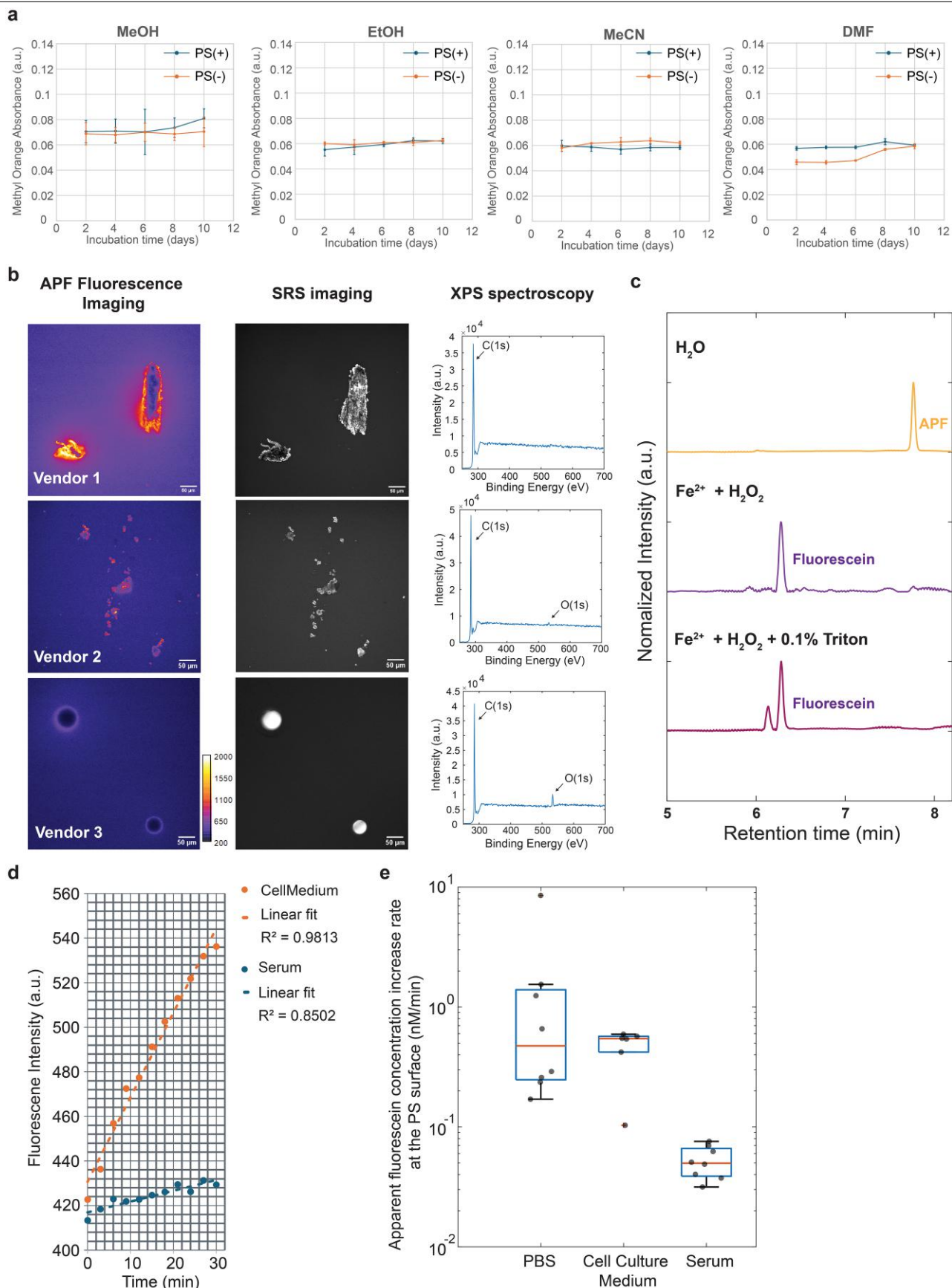
Additional information

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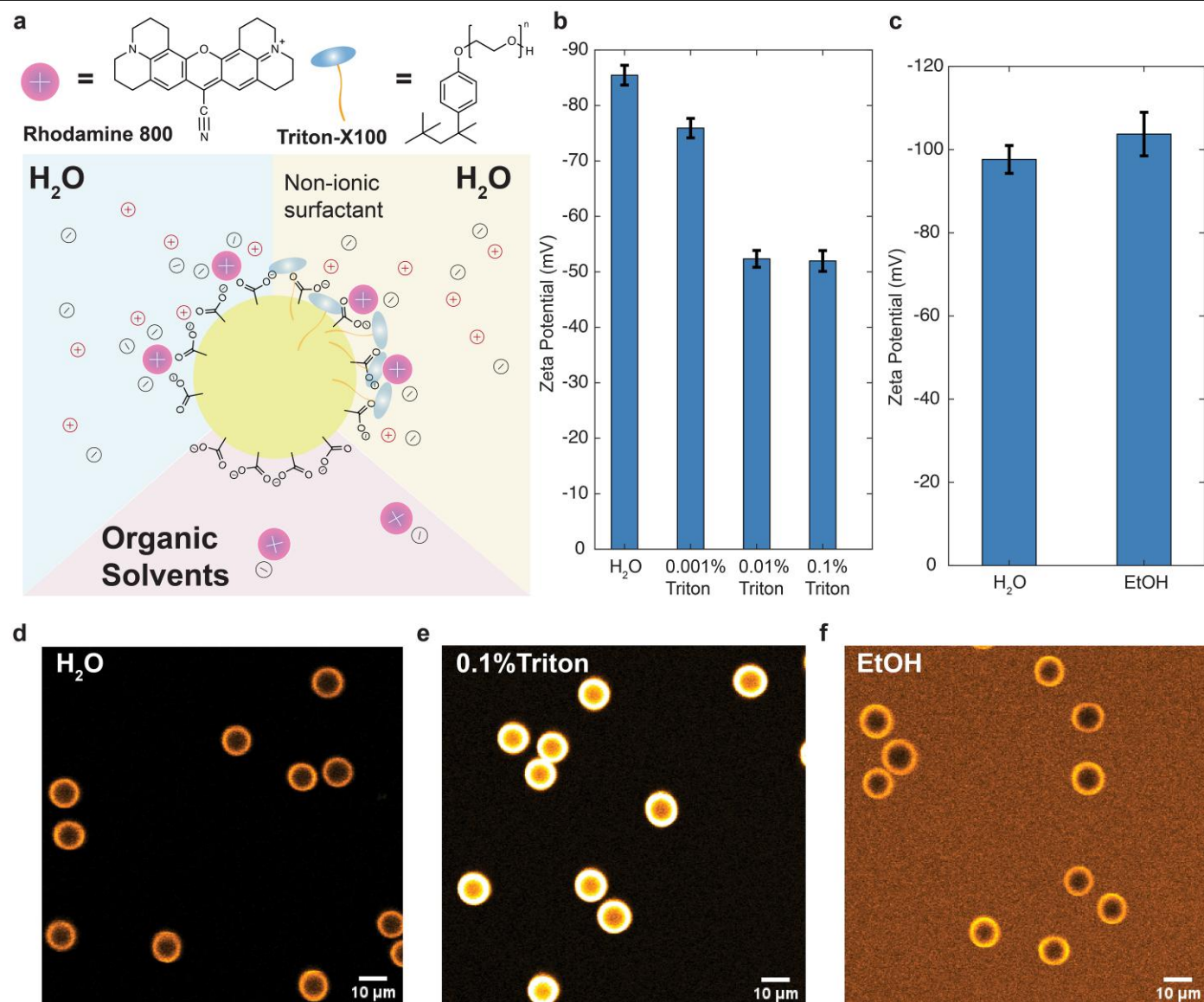
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Extended Data Fig. 1 | See next page for caption.

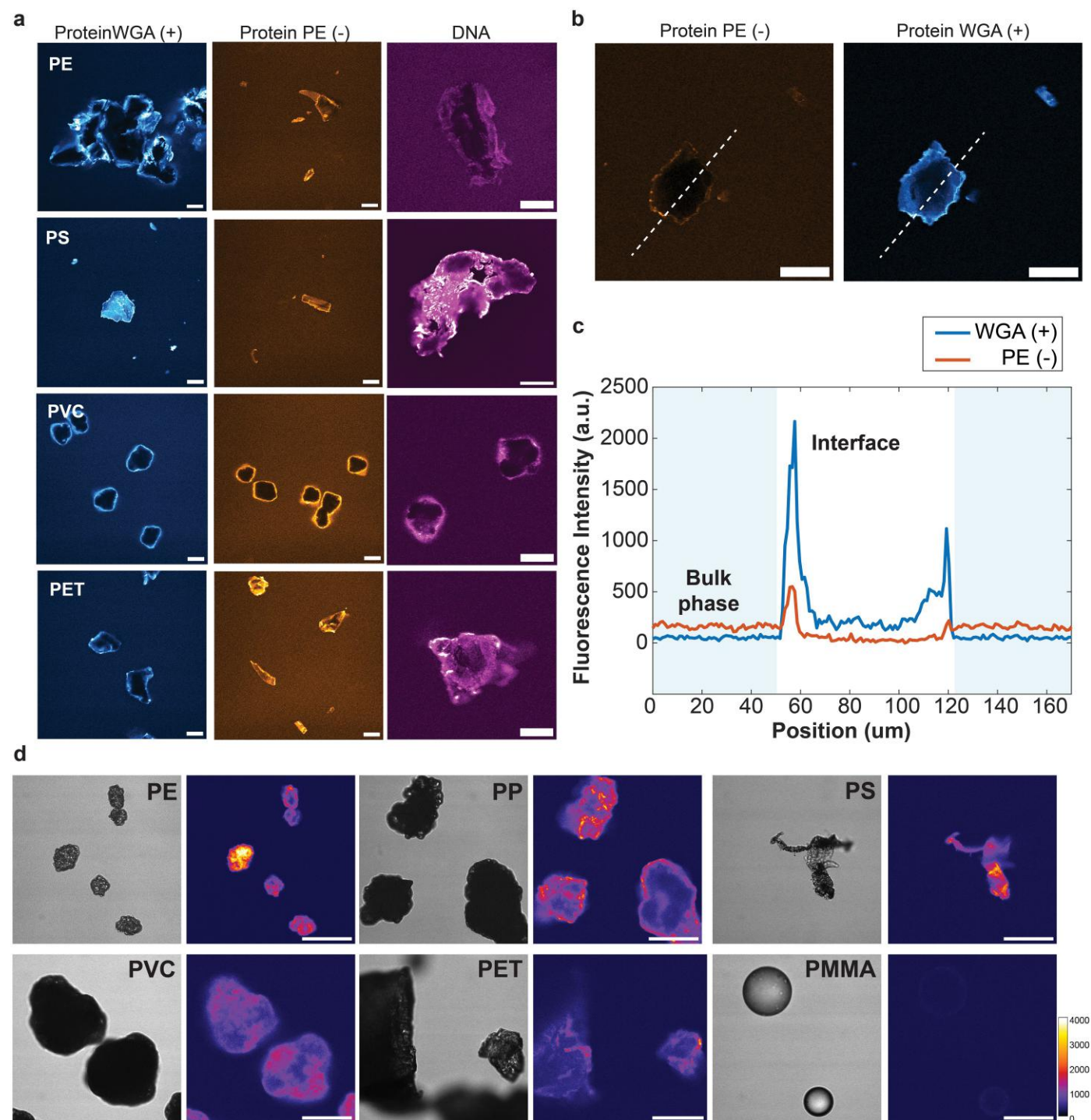
Extended Data Fig. 1 | Solvent dependence, generality, and apparent rates of hydroxyl radical generation at water-PS microplastic interfaces. **a**, Time tracking of methyl orange (MO) absorbance ($OD_{465nm} - OD_{700nm}$) with/without PS microplastics in MeOH, EtOH, MeCN, and DMF. While MO spectra vary slightly among solvents, this measurement can follow MO degradation and correct for scattering contributions at 700 nm. No MO degradation occurred in organic solvents, unlike its complete degradation in water. Data are the mean $\pm$ s.d.; $n = 3$ aliquot measurements. **b**, Universal surface reactivity at PS-water interface in $\bullet$ OH generation. Surface reactivity and functionality are evaluated for PS from different vendors. Surface reactivity: APF fluorescence (left) shows spontaneous $\bullet$ OH generation at hydrophobic PS-water interfaces; stimulated Raman scattering images (middle) show PS C-H vibrations at 3050 cm^{-1} . Scale bar, $50\text{ }\mu\text{m}$. Surface functionality: PS microplastics may experience oxidative aging, which introduces oxygen-containing groups (e.g., C=O, O-H). This can be evaluated using XPS spectroscopy (right). PS from vendor 1, characterized by a pristine surface, served as the model sample in this work. Although all samples exhibited surface reactivity, it decreased with increasing oxidation; PS from vendor 2 and 3, enriched in oxygen-containing groups, were less hydrophobic and showed reduced activity. **c**, HPLC analysis of APF reacting

with $\bullet$ OH with/without Triton X-100. APF showed no conversion in water (top; negative control), whereas the Fenton-generated $\bullet$ OH converted APF to fluorescein (middle; positive control). Adding Triton X-100 into Fenton reagent did not inhibit APF reaction with $\bullet$ OH, indicating the observed APF signal in Fig. 1i results from Triton's interactions with PS-water interfaces to modulate the surface reactivity (bottom). The top panel shows data representative of 5 independent experiments; the middle and bottom panel each show data from one independent experiment. **d-e**, Semi-quantitative estimation of apparent $\bullet$ OH production rate at PS-water interfaces under different environments. **d**, Representative time-dependent APF fluorescence measured at individual PS particle surfaces under different solution environments from measurements of $n = 6$ and $n = 8$ particle regions, respectively. The surface-associated fluorescence increase is largely linear over the measurement window, supporting the use of linear fitting to extract the rate of fluorescence increase for each particle. **e**, Apparent interfacial fluorescein generation rates at PS surfaces in PBS, cell culture medium, and serum, calculated by converting fluorescence increase rates into apparent generation rates using solution-specific calibrations. Each point represents one measured particle region; $n = 8, 6$ and 8 for PBS, cell culture medium, and serum, respectively.



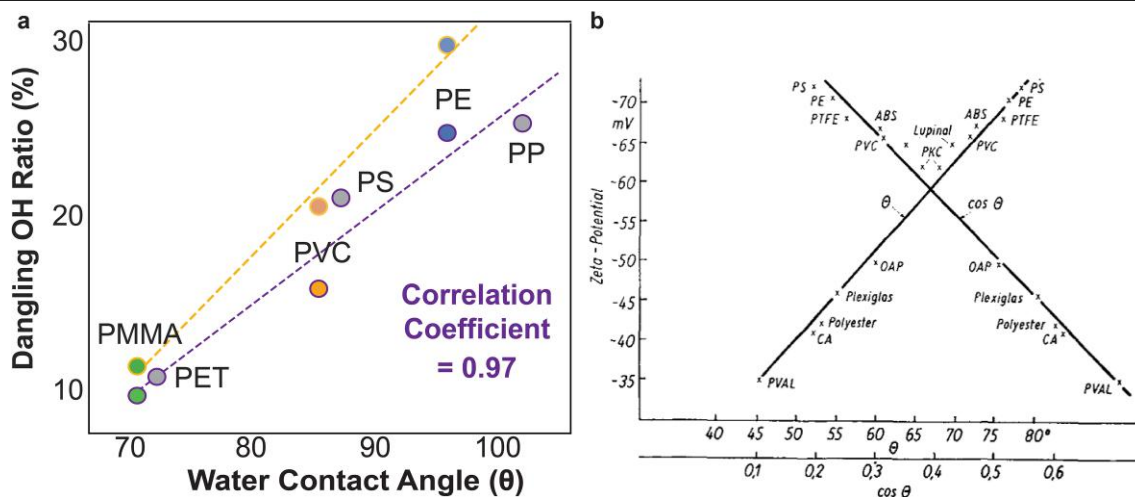
Extended Data Fig. 2 | Surface electrostatics of carboxylic acid-functionalized PS microparticles. **a**, A diagram illustrating different surface electrostatics of carboxylic acid functionalized PS microplastics in different solvent environments. **b**, Zeta potential of carboxylic acid functionalized PS microplastics in 1 mM NaCl containing 0%, 0.001%, 0.01% or 0.1% Triton X-100 ($n = 5$ independent measurements per concentration). **c**, Zeta potential of carboxylic acid functionalized PS microplastics in water ($n = 10$ independent

measurements) and ethanol ($n = 4$ independent measurements). Bars show the mean $\pm$ s.d. **d-f**, Fluorescence imaging of Rh800 localized on the surface of carboxylic acid functionalized PS microplastics (**d**) in water, (**e**) with Triton X-100, and (**f**) in ethanol environment. The negative surface charge of PS microplastics arising from oxygen-containing functional groups, such as carboxylic acids, shows distinct insensitivity to solvent conditions compared to the negative charges originating from water-hydrophobe interactions.



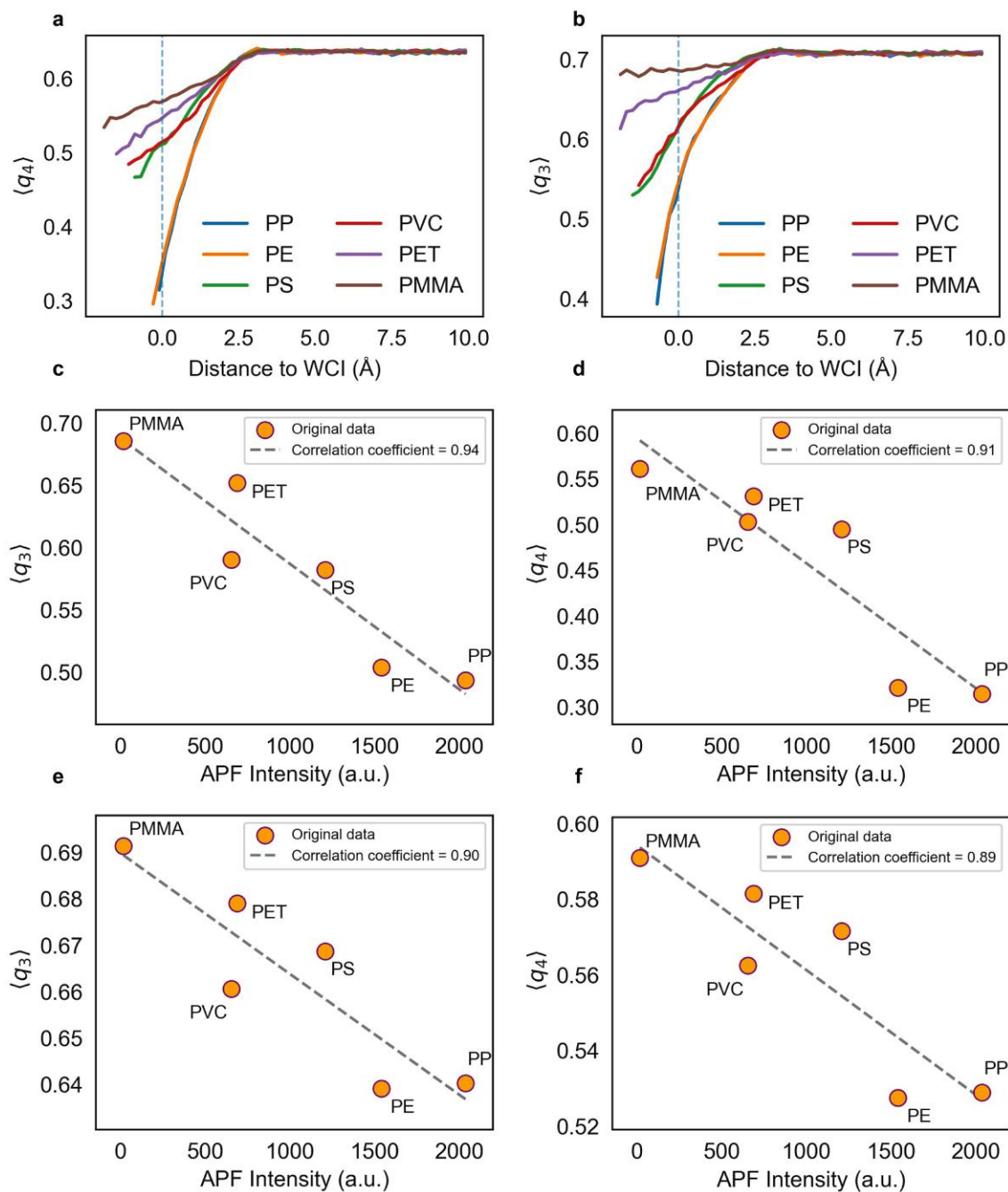
Extended Data Fig. 3 | Biomolecular adsorption on different commodity plastics, its charge dependency and protein aggregation at hydrophobic plastic-water interfaces. a, Confocal fluorescence images of surface localization of charged biomolecules including proteins and DNA at different hydrophobic plastic-water interfaces. Scale bar: 50 μm. **b-c**, Simultaneous imaging of the different surface partition of positively charged and negatively charged proteins. **b**, Simultaneous confocal fluorescence imaging of surface partition of negatively charged R-PE (left) and positively charged WGA-Alexa 647 conjugate (right). WGA conjugated with Alexa Fluor 647 was imaged in the far-red channel, excited by an LD laser (635 nm) with fluorescence collected

between 655–755 nm. R-phycoerythrin (R-PE) is imaged in the red channel, excited by a HeNe(G) laser (543 nm) with emission collected between 560–620 nm. Simultaneous imaging of the two channels reveals the different partition pattern of proteins of different charges on plastic surfaces. **c**, Line profile of the fluorescence intensity at the corresponding dash line in panel **b**. **d**, Protein aggregation at plastic-water interface. Confocal images of the fluorogenic Thioflavin T on the surface of microplastics are shown in pair with the corresponding brightfield images of plastic particles in PBS. Scale bar: 50 μm.



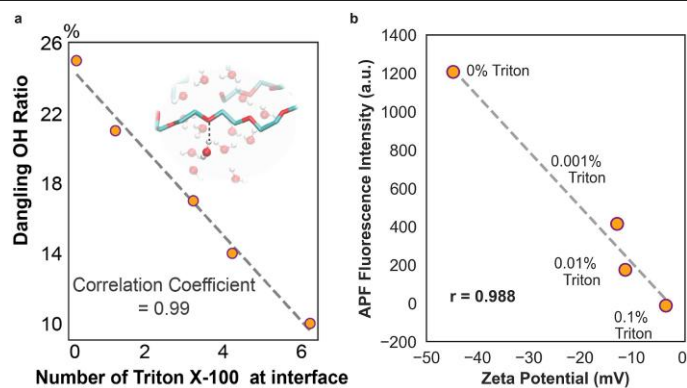
Extended Data Fig. 4 | Hydrophobicity of microplastics governs their water contact angle and surface electrification. a, Microplastic-water interface hydrophobicity quantified by contact angle. Simulated ratio of surface dangling OH groups (defined as water without any acceptor (X) with in an intermolecular O...X distance less than 3.5 Å and with an H-O...X angle (β) smaller than 50°) versus water contact angle. Water contact angle (θ) reported from Accu Dyne Test™ Surface Energy Database³⁷. **b,** Surface electrostatics

from water electrification correlates with hydrophobicity at plastic-water interface³⁵. All polymers show negative surface potential, with hydrophobic ones exhibiting stronger negativity. Polyolefins without polar groups are more hydrophobic and negatively charged than polymers bearing hydrophilic functionalities such as esters. Figure adapted with permission from ref. 35, Wiley.

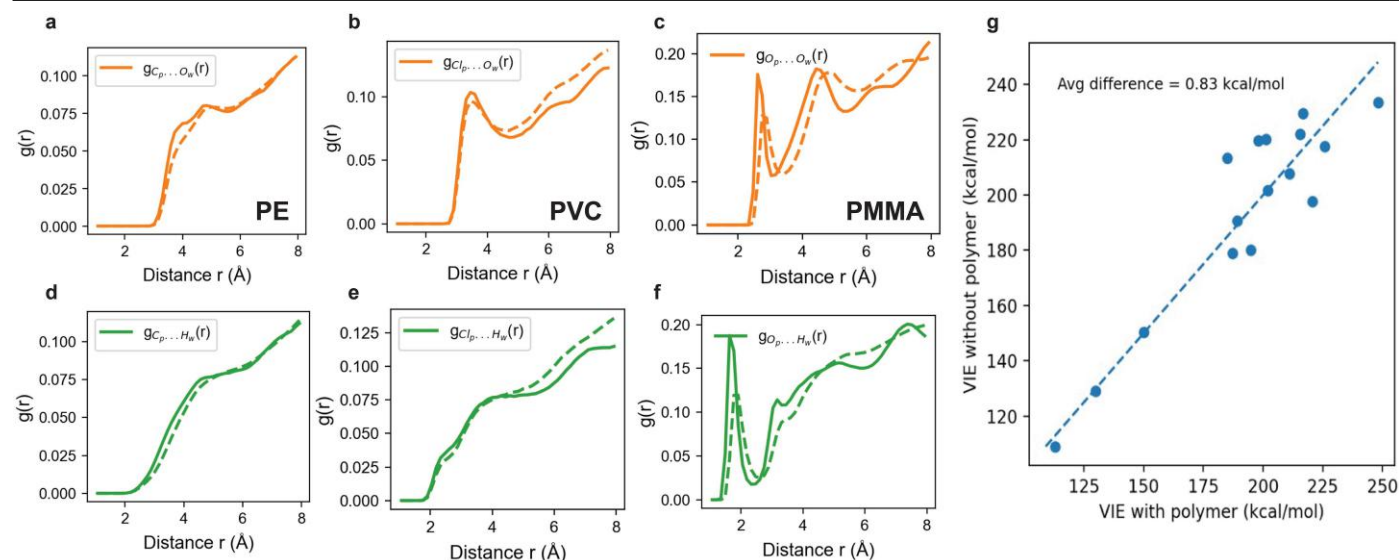


Extended Data Fig. 5 | Microplastic-water interface hydrophobicity quantified by tetrahedral order. **a-b.** Average values of order parameters **a)** $\langle q_4 \rangle$ and **b)** $\langle q_3 \rangle$ for water as a function of distance to the WCI. The vertical blue line represents WCI. **c-f.** Correlation between interfacial water tetrahedral order ($\langle q_3 \rangle$, $\langle q_4 \rangle$) and chemical activity (APF fluorescence at the particle surface) across six water-plastic interfaces. **c-d.** Averaged **c)** $\langle q_3 \rangle$ and **e)** $\langle q_4 \rangle$ for waters located on

the plastic side of the Willard-Chandler interface (distance to WCI < 0 Å). **e-f.** Averaged **e)** $\langle q_3 \rangle$ and **f)** $\langle q_4 \rangle$ for waters on the aqueous side within 0–2 Å of the WCI. Hydrophobic surfaces lower tetrahedral order relative to bulk, indicating a more defective interfacial H-bond network. The reduction of tetrahedral order is strongest for PE and PP, consistent with their higher hydrophobicity, whereas PMMA and PET are more bulk-like.

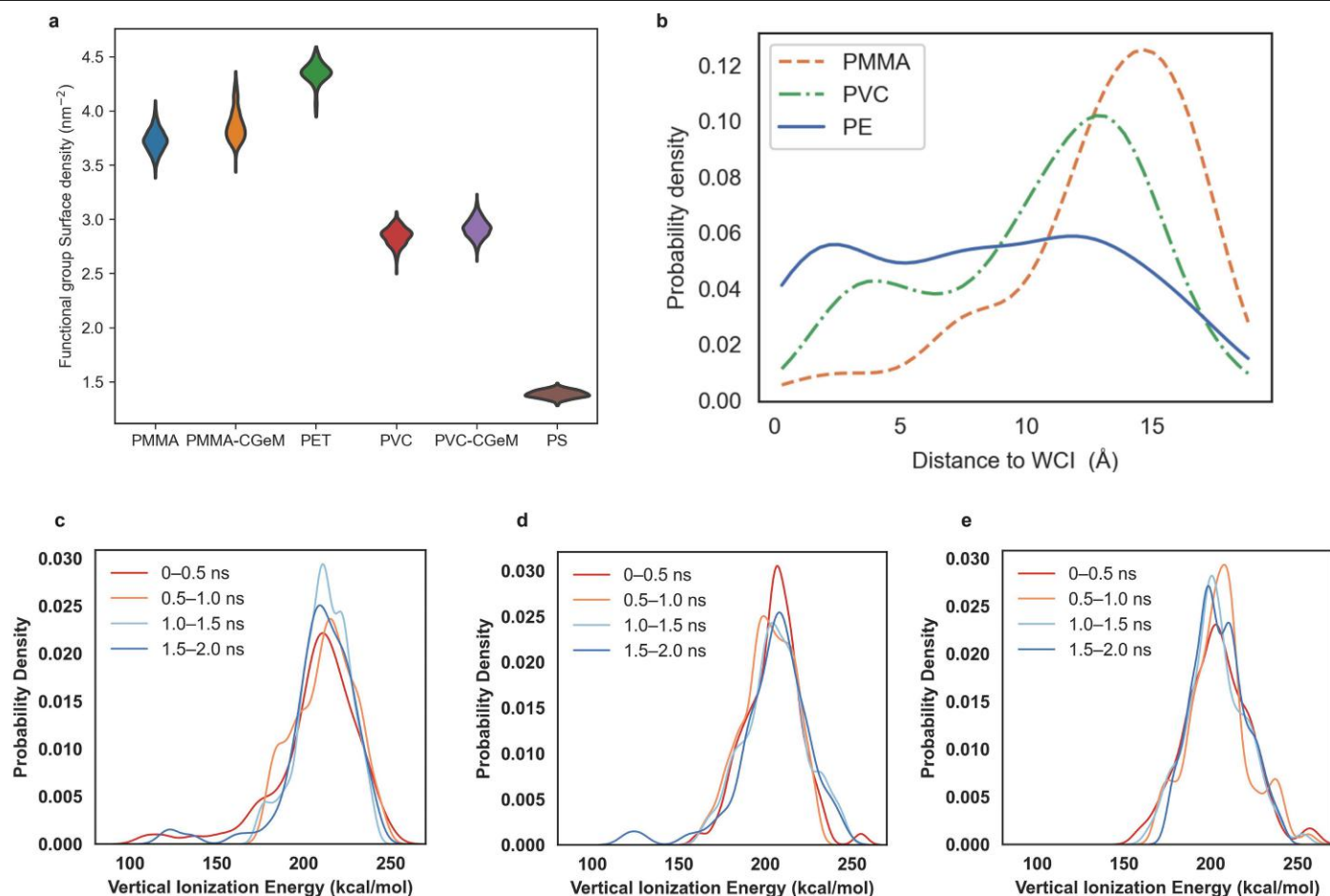


Extended Data Fig. 6 | PS microplastic-water interfaces modulated by different Triton X-100 concentrations. a. Correlation between simulated dangling OH ratios and added Triton X-100 surfactants. **b.** Correlation between surface electrostatics and chemical reactivity indicated by APF assay for PS microplastics in water supplemented at different concentrations of Triton X-100.



Extended Data Fig. 7 | Validation of the hybrid force-field description and VIE calculation protocol. **a-f**, Radial distribution functions between polymer surface atoms and water molecules for PE, PVC, and PMMA systems. Top panels (**a-c**) show $g_{\text{polymer} \dots O_w}(r)$, and bottom panels (**d-f**) show $g_{\text{polymer} \dots H_w}(r)$. For PE, carbon atoms are used as representative surface sites; for PVC, chlorine atoms; and for PMMA, the carbonyl (COOR) oxygen atoms. Solid and dashed

lines correspond to different force-field descriptions (OPLS-AA/C-GeM and OPLS-AA/SPC/E, respectively). **g**, Comparison of VIE values computed with and without inclusion of the PE polymer configurations. Each point corresponds to an individual configuration. The close agreement between the two sets of results indicates that polymer inclusion has a negligible effect on the computed VIE.



Extended Data Fig. 8 | Polymer-dependent interfacial structure, hydroxide coordination, and VIE distributions. **a**, Surface density distributions of exposed functional groups for different polymer systems. Functional groups are defined as atoms or motifs located within 4 $\text{\AA}$ of the WCI. Representative groups include Cl atoms for PVC, the two oxygen atoms (COOR) for PET and PMMA, and aromatic ring centroids for PS. Results obtained using OPLS-AA/SPC/E for PMMA, PET, PVC, and PS, and OPLS-AA/C-GeM for PMMA and PVC are shown for comparison. The narrow distributions indicate minimal fluctuation in surface composition, consistent with a structurally stable interface. **b**, Probability distributions of undercoordinated hydroxide ions as a function of distance to WCI for water-PE, water-PVC, and water-PMMA systems.

The distributions reveal that undercoordinated hydroxide ions in water-PE are more broadly distributed and extend closer to the interface, whereas in PMMA they are shifted further away from the interface. PVC exhibits intermediate behavior between the two systems. **c-e**, Time-resolved VIE distributions of interfacial hydroxide at the water-polymer interface for (c) PE, (d) PVC, and (e) PMMA over a 2 ns simulation. Each curve corresponds to a 500 ps trajectory segment (0–0.5 ns, 0.5–1.0 ns, 1.0–1.5 ns, and 1.5–2.0 ns), with configurations sampled every 5 ps. The overall consistency of the distributions across successive segments indicates that the VIE statistics are well converged over the simulation timescale.

Extended Data Table 1 | Fluorescence response of APF to various reactive oxygen species (ROS)

Reactive Oxygen Species (ROS)	ROS Generation Method	APF Fluorescence
Hydrogen peroxide (H ₂ O ₂)	100 μM H ₂ O ₂	<1
Hydroxyl radical (HO•)	100 μM ferrous perchlorate (II) and 1 mM of H ₂ O ₂	1200
Peroxyl radical (ROO•)	100 μM 2,2'-azobis(2-amidinopropane), dihydrochloride (AAPH)	<1
Singlet oxygen (¹ O ₂)	100 μM 3-(1,4-dihydro-1,4-epidioxy-1-naphthyl)propionic acid	9
Superoxide anion (•O ₂ ⁻)	100 μM KO ₂	6
Autooxidation	2.5 hours exposure to fluorescent light source	<1

Values represent relative fluorescence intensity after probe oxidation by different ROS, illustrating the distinct selectivity of the probe. Data from ref. 68.