Direct observation of water-mediated single-proton transport between hBN surface defects

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Aqueous proton transport at interfaces is ubiquitous and crucial for a number of fields, ranging from cellular transport and signalling, to catalysis and membrane science. However, due to their light mass, small size and high chemical reactivity, uncovering the surface transport of single protons at room temperature and in an aqueous environment has so far remained out-of-reach of conventional atomic-scale surface science techniques, such as scanning tunnelling microscopy. Here, we use single-molecule localization microscopy to resolve optically the transport of individual excess protons at the interface of hexagonal boron nitride crystals and aqueous solutions at room temperature. Single excess proton trajectories are revealed by the successive protonation and activation of optically active defects at the surface of the crystal. Our observations demonstrate, at the single-molecule scale, that the solid/water interface provides a preferential pathway for lateral proton transport, with broad implications for molecular charge transport at liquid interfaces.

Proton transport in bulk water is known to occur via the so-called Grothuss mechanism, whereby protons tunnel between individual water molecules along liquid wires formed by hydrogen bonds. This remarkable transport mechanism, postulated almost 200 years ago, explains the anomalous and peculiarly high mobility of hydronium and hydroxide ions in bulk water. At interfaces, the situation is much more complex, with experimental and theoretical efforts pointing to a wealth of effects, ranging from specific proton desorption barriers potentially facilitated by interactions with water molecules and hydrogen bonding, peculiar charging effects due to water negative self-ion, to two-dimensional (2D) confinement of protons at hydrophobic interfaces, leading to facilitated lateral transport. However, interferential transport of protons, and its relationship with the surrounding aqueous water environment has so far remained elusive, due to a lack of direct measurements at the single-molecule scale and under environmental conditions. A finer molecular understanding of proton transport at interfaces would have fundamental importance for a range of fields and materials, from cell membranes in biology and solid-state interfaces.

As shown in Fig. 1a, our sample is composed of multilayer boron nitride flakes, exfoliated from high-quality crystals. Such exfoliated hBN flakes are atomically smooth and host very few intrinsic defects. As shown in Fig. 1b–d, we observe a drastic change to the photoluminescence response of the hBN flake when exposed to air (i), black) or to aqueous solutions of varying acidity (ii), blue, and (iii), red, corresponding to pH 9.8 and pH 3.4, respectively, pointing to the high reactivity of surface defects in aqueous conditions. Figure 1b shows the wide-field image of the hBN flake under uniform illumination, with the flake physical boundary highlighted as a white contour. For each frame, emission originating from optically active defects at the surface of the flake, which is characterized by uniform emission at 585 nm (2.08 eV), consistent with previous reports (Supplementary Fig. 1). Remarkably, as shown in Fig. 1b–d, we observe a drastic change in the photoluminescence response of the hBN flake when exposed to air (i) or to aqueous solutions of varying acidity (ii), blue, and (iii), red, corresponding to pH 9.8 and pH 3.4, respectively, pointing to the high reactivity of surface defects in aqueous conditions. Figure 1b shows the wide-field image of the hBN flake under uniform illumination, with the flake physical boundary highlighted as a white contour. For each frame, emission originating from the optical excitation source is detected at the surface of the flake.
We observe, in Fig. 1c, that while only few defects are active in air, a large number of defects are homogeneously activated in aqueous conditions (air, or water solutions of varying acidity). Inset: zoomed-in view of a surface defect (protonated boron vacancy $V_\text{BH}$), surrounded by water molecules. Boron, nitrogen, oxygen and hydrogen atoms are represented as blue, green, red and white, respectively. a, hBN crystal containing irradiation-induced surface defects is illuminated by a continuous green laser, leading to localized emission from optically active defects (red). The crystal can be exposed to various environmental conditions (air, or water solutions of varying acidity). Inset: zoomed-in view of a surface defect (protonated boron vacancy $V_\text{BH}$), surrounded by water molecules. Boron, nitrogen, oxygen and hydrogen atoms are represented as blue, green, red and white, respectively. b–d, Larger defect reactivity in aqueous acidic conditions, comparing flake in (i) air, (ii) in basic (pH 9.8) and (iii) acidic (pH 3.4) water solutions. b, Wide-field image of an hBN flake, obtained with 20 ms exposure time. Emission from individual surface defects (highlighted by red and blue circles) can be localized with ~5–40 nm uncertainty (see Supplementary Discussion 1.2). Scale bar, 5 μm. c, Reconstructed super-resolved images of the flake surface (Supplementary Discussion 1.3). Scale bar, 1 μm. d, Number, $N$, of emissive defects per frame as a function of time for the three environmental conditions. In air, the number of active defects is consistently small. In water, we observe a large number of active defects upon illumination, which decreases to reach a steady state (dashed box, see Supplementary Discussion 2 and Supplementary Fig. 5 for analysis of the relaxation kinetics). Inset shows the histogram of the number of active defects per frame at steady state, fitted by Poisson distributions. Vertical lines in the inset show the average number of defects per frame. A larger activity of surface defects is evidenced in acidic conditions, consistent with protonation-induced activation of defects. e, Three-state model for the protonation-induced transition between non-emissive negatively charged boron vacancy $V_\text{B}^-$, and emissive neutral protonated boron vacancy $V_\text{BH}$, with excited state $V_\text{BH}^*$ (Supplementary Fig. 4).

From surface defects can be localized with subwavelength uncertainty, with a typical localization uncertainty $\sigma_\text{LOC} \approx 5–40$ nm, scaling as $\sigma_\text{LOC} \approx \sigma_\text{PSF}/\sqrt{N_\text{ef}}$, with $\sigma_\text{PSF} \approx 150$ nm fixed by the point spread function of the microscope and $N_\text{ef}$ the number of emitted photons (Fig. 1b, blue and red circles show localized defects, also see Supplementary Discussion 1.2). Consecutive localization of emitters over successive frames (here 20,000) allows us to reconstruct a super-resolved spatial map of the defects at the surface of the crystal, with a zoomed-in view on a $2 \times 2 \mu$m² area shown in Fig. 1c. We observe, in Fig. 1c, that while only few defects are active in air, a large number of defects are homogeneously activated in aqueous conditions (Supplementary Fig. 9 for super-resolved maps of the entire flake). This difference is also highlighted by monitoring the number, $N$, of emissive defects per frame under illumination (Fig. 1d). In air, the number of active defects per frame is consistently low, with $\langle N \rangle \approx 0.3$ active defects per frame. Immersing the flake in water, we observe upon illumination a very large number of active defects (here $N \approx 70$, corresponding to ~1 active site per μm²), pointing to the activation of defect luminescence due to solvent molecules (Supplementary Fig. 9). The number of active defects decreases upon illumination over tens of seconds (Supplementary Figs. 3 and 5) to reach a steady state, characterized by $\langle N \rangle \approx 1–4$ active defects per frame. Importantly, the luminescent state of defects is recovered over sufficiently long dark periods, as well as through successive drying and wetting steps (Supplementary Figs. 6 and 7).

Varying water acidity further allows us to identify environmental protons, $H^+$, as being the chemical species responsible for the activation of defect luminescence. Comparing the two pH conditions in Fig. 1b–d, we indeed observe an increase by a factor of ~2 in the number of emissive defects at acidic pH (Fig. 1d, inset), as well as an increase in the density of activated emitters (Fig. 1c). This monotonic increase in defect activity under acidic conditions was systematically observed in all the investigated crystals over 12 pH units (Supplementary Fig. 10).

To rationalize our observations, we perform ab initio molecular dynamic simulations of a defective hBN interface in water (Fig. 1a, inset, Supplementary Discussion 5 and Supplementary Video 1). On the basis of recent simulations on anhydrous bulk hBN defects and high-resolution transmission electron microscopy images of hBN monolayers and single layers, we probed the reactivity of boron monovacancy complexes in water, namely, $V_\text{B}^-$ (identified as the likely 2 eV emitter) and $V_\text{BH}$ (non-emissive at 2 eV, having a lower acceptor defect state in the gap). Our simulations demonstrate that solvated aqueous protons behave like charge-compensating centres and incorporate easily on the negatively charged defect $V_\text{B}^-$, through $V_\text{B}^- + H^+ \Rightarrow V_\text{BH}$, which is consistent with the large activation of luminescence observed in the aqueous environment.
These numerical observations allow us to propose the phenomenological three-state model depicted in Fig. 1e. In the absence of illumination, the number of protonated defects is fixed by the acid–base equilibrium $\text{V}_H^+ + \text{H}^+ \leftrightarrow \text{V}_BH$. Probing this equilibrium experimentally, we determine a $K_a \geq 14$, consistent with the strong basicity evidenced by the simulations (Supplementary Fig. 8). Upon illumination, defects in the protonated state are converted to their excited state $\text{V}_BH^*$, from which they can either decay radiatively back to the ground state $\text{V}_BH$, or lose their protons to be converted back to $\text{V}_H^+$, through an excited-state proton transfer35 (Supplementary Fig. 4). This second non-radiative pathway leads to the initial decrease of the number of active defects upon illumination (Fig. 1d and Supplementary Fig. 5) by effectively shifting the chemical equilibrium between $\text{V}_H^+$ and $\text{V}_BH$, reaching a second steady-state level under constant laser illumination. This photoacidic behaviour is consistent with the relative excited-state energy levels of the protonated and deprotonated defect33 (Supplementary Fig. 4). Consistently, a decrease in the number of active defects at steady state is observed for increasing illumination power (Supplementary Fig. 11). This ON/OFF transition between distinct protonation states, reported here for defects in hBN, is commonly observed for fluorescent dyes36,37. Note, finally, that while our observations and ab initio simulations are consistent with the $\text{V}_H^+/\text{V}_BH$ transition between emissive and non-emissive states, other types of defects with nitrogen-dangling bonds and distinct protonation states could also be responsible for these observations.

**Luminescence migration reveals proton trajectories**

Since the defects are emissive in their protonated form, monitoring luminescence events at the surface of the flake allows us to directly track down the spatiotemporal dynamics of defect protonation. Figure 2a shows the temporal evolution over 600 ms of the luminescence in a $1 \times 1 \mu\text{m}^2$ region at the surface of a flake immersed in de-ionized water (pH $\sim$5.5), with subpixel localization of the position of the emitter shown as the red cross. As highlighted in this sequence of images, a single diffraction-limited luminescence spot spatially wanders between successive frames over a total distance of $\sim 500 \text{ nm}$. Consecutive localizations allow us to reconstruct the position of successively activated defects, shown as the red line trace in Fig. 2a and the reconstructed trajectory in Fig. 2b, with a radius corresponding to uncertainty in localizations. The observation of the consecutive activation of luminescence of nearby defects over 30 successive frames points to the presence of a single activating excess proton hopping from defect to defect (Fig. 2c, inset), and leading to the observed spatiotemporal activation of luminescence. Importantly, monitoring defect activation over the whole flake allows us to discard artefacts in these observed trajectories related to stage drift or random activation of emitters (Supplementary Figs. 14 and 15). As schematically represented in Fig. 2c, this observed sequence of correlated luminescence events must then correspond to (i) the adsorption of a proton at the site of one defect, leading to the appearance of a luminescence spot at the surface of the flake (Fig. 2a, $t=0 \text{ ms}$), followed by (ii) hopping of the excess proton between nearby surface defects over the total residence time $T_{\text{BH}}$ with successive hopping length $\delta l$ and (iii) the desorption of the proton from the flake surface, leading to extinction of luminescence (Fig. 2a, $t=620 \text{ ms}$). Importantly, we demonstrate through simulations that such correlated luminescence events and trajectories cannot stem from the random activation of emitters at the surface, and must correspond to the correlated transfer of single excess proton between defects (Supplementary Discussion 3.2). Following the three-state model of Fig. 1e, the variation in luminescence intensity observed between successive frames could stem from fluctuations between radiative and non-radiative recombination of the excited defects, for example, due to transient proton unbinding and geminate recombination18. Albeit in a different context, the concepts presented here for single-proton tracking are similar to strategies explored in single-molecule and single-enzyme catalysis18–45.

**Interfacial mobility and desorption-limited transport**

These correlated proton trajectories occur consistently and repeatedly upon constant illumination (Supplementary Video 2). We track and analyse their dynamics using standard single-particle tracking techniques46, focusing on the steady-state regime with a constant averaged density of active defects per frame of $\sim 0.1–1$ per $10 \mu\text{m}^2$ (Fig. 1d, dashed boxes). Individual trajectories are defined...
by correlating localizations less than ~300 nm apart between successive time frames. This threshold is rigorously defined by measuring the statistic of hopping length $l$ (Supplementary Fig. 13). Importantly, this tracking methodology is robust with respect to the correlation length and sampling time and is validated against simulations of random activation of emitters (Supplementary Fig. 14). As shown in Fig. 3, ~1700 individual trajectories longer than 200 ms (ten successive frames) can be successfully identified over 180 s (Supplementary Video 2). Representative trajectories are highlighted in Fig. 3a–c (see also Supplementary Fig. 19 and Supplementary Videos 4–8). Remarkably, a large heterogeneity is observed between distinct trajectories at the single-molecule scale. Some excess protons remain at a fixed position (Fig. 3a), while others migrate up to 1 μm (Fig. 3b,c and Supplementary Fig. 19). Long adsorbing steps (40–100 ms) within one uncertainty-limited defect, separated by relatively long hopping events (50–200 nm), are also observed in some trajectories (red dashed circles, Fig. 3c). For each individual trajectory, we can compute the associated square displacement $SD(t) = (X(t) - X(t = 0))^2$, which characterizes the diffusive character of these random walks. From the initial increase of the square displacement with time, one can extract a diffusion coefficient $D$ for each individual trajectory, as $SD = 4Dt$ (dashed line in the SD graphs), which is found to be $D_{(a)} \approx 10^{-16} \text{m}^2\text{s}^{-1}$ (no diffusion), $D_{(b)} \approx 8 \times 10^{-14} \text{m}^2\text{s}^{-1}$ and $D_{(c)} \approx 25 \times 10^{-14} \text{m}^2\text{s}^{-1}$, respectively. Note that the larger number of observed trajectories at the edges might be due to a larger density of defects (see Supplementary Fig. 27).

As shown in Fig. 4a, we characterize the interfacial mobility of protons at the surface of the flake through the evolution of the mean square displacement (MSD) averaged over all observed trajectories (the averaged MSD $= \langle (X(t) - X(t = 0))^2 \rangle$) is a well-defined quantity, independent of sampling time and tracking parameters, see Supplementary Discussion 3). As shown in Fig. 4a, the MSD follows an initial linear increase, characteristic of a standard diffusive behaviour at short times ($t < 300$ ms), followed by a subdiffusive behaviour at longer times, which is possibly due to longer adsorbing events at some defect sites. The linear regime allows us to define the average diffusion coefficient $D = 2.8 \times 10^{-14} \text{m}^2\text{s}^{-1}$, and is typically found to be of the order of $10^{-14} \text{m}^2\text{s}^{-1}$ for the majority of flakes. We further show, in the inset, the broad distribution of diffusion coefficients from individual single-molecule trajectories, with a noticeable proportion of trajectories characterized by no net observed motion ($D < 1 \times 10^{-14} \text{m}^2\text{s}^{-1}$, as in Fig. 3a). To analyze the statistics of these bidimensional proton walks in more detail, we plot in Fig. 4b,c the distribution of hopping length $l$ and residence time $T_R$ at the surface (calculated as $T_R = N_R \Delta t$, where $N_R$ is the trajectory length in frames and the sampling time $\Delta t = 20$ ms). Those distributions are well approximated by power laws, $N(l) \approx l^{−β}$ and $N(T_R) \approx T_R^{−ν}$, with values of $ν \approx 2.6$ and $μ \approx 1.6$ in this case, and values that are found typically in the range $ν \in [2.4 - 4]$ and $μ \in [1.6 - 2.5]$ (Supplementary Fig. 13). The power-law scaling for the jump length $l$ is reminiscent of Levy-type processes and demonstrates the anomalous non-Brownian character of these hopping events, due to the finite distance between randomly distributed defects (defect density on this flake can be estimated to be at least $500 \mu m^{-2}$, leading to an averaged interdefect distance of 40 nm). The power-law scaling of the residence time naturally arises from the length of a diffusion-controlled escape process, and is larger than for normal diffusion, for which $μ = 1.5$. Importantly, a large fraction (~70%) of protons remains on the surface of the flakes between each frame, leading to trajectories that are subsequently analysed (Supplementary Fig. 20).

The orders of magnitude difference between the measured diffusion coefficient for proton surface transport, $D ≈ 10^{-14} \text{m}^2\text{s}^{-1}$, and the hydronium diffusion coefficient in the bulk $D_{\text{H}_2\text{O}} ≈ 10^{-8} - 10^{-7} \text{m}^2\text{s}^{-1}$, and at biological membranes $D_{\text{membrane}} ≈ 10^{-11} - 10^{-9} \text{m}^2\text{s}^{-1}$, suggests the presence of a strong rate-limiting step for interfacial proton transport. We thus compare the surface transport of the two isotopes, hydrogen and deuterium (Fig. 4d, comparing transport in H_2O and D_2O in a distinct flake, see also Supplementary Fig. 22). As shown in Fig. 4d, diffusion is hindered in D_2O by at least a factor of 4 compared with H_2O. This isotopic hindrance to diffusion is larger than the factor of 1.5–2 that one would expect from hindrance of either Grotthuss-like proton transfer or self-diffusion$^{5,6}$, pointing to desorption from defects rather than transport between nearby defects as the rate-limiting step for excess proton transport. Such desorption-limited transport is consistent with the low value of the interfacial diffusion coefficient, the large distribution in diffusion coefficients observed in individual trajectories (Fig. 4a, inset), as well as the long adsorbing steps.
evidenced at some defect sites (Fig. 3, trajectories (a) and (c)). Note, finally, that this hindered desorption-limited transport validates a posteriori the choice of our spatiotemporal resolution and tracking parameters (\(\Delta t = 10 - 20\) ms and \(\Delta l = 300\) nm) for which the largest measurable diffusion coefficient is \(D = 2.8 \times 10^{-14} \text{m}^2\text{s}^{-1}\). Inset shows the distribution of the diffusion coefficient determined on individual trajectories, with the vertical dashed line being the averaged diffusion coefficient. This value, despite being smaller than the bulk hydronium diffusion coefficient, remains two orders of magnitude larger than the desorption-limited interfacial diffusivities, allowing us to consistently measure and characterize the hindered interfacial proton transport between defects (Supplementary Discussion 3). Additional characterization of the proton transit time between defects (corresponding to unhindered interfacial proton transport) would require a temporal resolution \(\delta t \approx 1 \mu\text{s}\) at this 100-nm scale, which is unreachable even with state-of-the-art single-molecule tracking techniques.

On the basis of these insights, we can, for desorption-limited transport, express the diffusion coefficient as \(D = \frac{1}{\tau} \langle v \rangle^2\), with \(\langle v \rangle (\text{s}^{-1})\) the jump rate and \(\tau\) the characteristic jump length between nearby defects. This jump rate scales as \(\nu \approx \nu_0 \exp\left(-\frac{\Delta F}{k_B T}\right)\), where \(\nu_0 (\text{s}^{-1})\) is a molecular frequency and \(\Delta F\) is the free-energy desorption barrier from the defect. As an order of magnitude estimate, we take the attempt frequency as \(\nu \approx 1/\tau\), with \(\tau\) the order of nanoseconds corresponding to the excited-state lifetime (Supplementary Fig. 2), and \(a \approx 10 - 100\) nm, leading to a typical desorption energy barrier of \(16 - 20\) \(k_B T \approx 0.4 - 0.5\) eV. As shown in Fig. 4c, we indeed observe an increase in proton mobility with increasing temperature, from which we extract a mean activation energy \(\Delta E \approx 0.62 \pm 0.12\) eV, demonstrating the predominantly enthalpic nature of this free-energy barrier (Supplementary Fig. 28). This barrier then characterizes the energy necessary to break the NH covalent bond from the excited defect \(V_{_{\text{NH}}}^n\) and for the solvated \(H^+\) to escape the electrostatic attraction of the negatively charged vacancy \(V_{_{\text{B}}}^n\). Consistently, this barrier is much smaller than the hydrogen removal energy of \(> 2.34\) eV predicted to break the NH bond from the \(V_{_{\text{NH}}}^n\) defect in gas phase, as the proton desorption barrier might be reduced here by the presence of nearby hydrogen-accepting water molecules, as well as by the laser irradiation. Indeed, we did not observe any proton mobility in air (Supplementary Fig. 26), despite the presence of adsorbed water at the flake surface in ambient conditions (40% relative humidity), demonstrating the crucial role of bulk water in mediating proton mobility at the surface of the flake and consistent with recent simulations. Desorption-limited transport is further confirmed by the weak dependence of mobility on illumination power (Supplementary Fig. 21). Furthermore, as shown in Supplementary Figs. 23 and 24, the presence of salt and dissolved gas does not noticeably affect the interfacial proton mobility, while we observed a net increase in mobility at low pH in a majority of flakes (Supplementary Fig. 25), consistent with increased defect activity and change of surface state. Finally, we note that the high purity and atomic flatness of the hBN surfaces should also lead to reduced probability of proton trapping at non-emissive sites, allowing direct observation of excess proton transport between nearby defects.

**Proton segregation at the solid/water interface**

The emerging picture is therefore that of a desorption-limited transport of protons between adjacent surface defects, mediated by the solid/water interface. While several experiments have reported evidence for interfacial proton mobility at surfaces through ensemble measurements, the trajectories observed here at the surface of the flake (Figs. 2 and 3) represent direct observation at the single-molecule scale of the interfacial segregation of proton excess at the solid/water interface, demonstrating that this interface provides a preferential pathway for charge transport. Indeed, in the absence of any free-energy barrier trapping protons at the interface, a proton irreversibly desorbing into the bulk would diffuse over \(\delta t \approx \sqrt{2D_{\text{bulk}} \cdot \delta t} \approx 300\) nm during the \(\delta t = 20\) ms sampling time, preventing any correlations in the activation of defects ~100 nm apart. The power-law tail of the surface residence time (Fig. 4c), concomitant with the finite diffusivity (Fig. 4a), accordingly demonstrates the large probability of near-surface charges remaining segregated and mobile at the surface. In-plane proton transport at the flake surface (Fig. 2c, step (ii)) must therefore be favoured compared to irreversible proton desorption into the bulk (Fig. 2c, step (iii)), due to the presence of an interfacial free-energy barrier leading to segregation of the excess protons at the hBN/water interface.
To probe the segregation of interfacial protons in more detail, we simulated the dynamics of a hydronium ion at the interface of water and pristine hBN (Fig. 4f). As observed in this 20-ps trajectory (Supplementary Video 9), the hydronium ion indeed remains segregated (physisorbed) at the interface, while keeping high lateral mobility through Grotthus transfer, with a lateral diffusion coefficient \(D \approx 8 \times 10^{-9} \text{ m}^2/\text{s}^2\) that is close to the bulk hydronium diffusion coefficient \(D_{\text{bulk}} \approx 10^{-8} \text{ m}^2/\text{s}^2\). As shown in the inset of Fig. 4f, computation of the free energy of the aqueous hydronium approaching a pristine hBN surface further confirms the presence of an interfacial \(-0.3\,\text{eV}\) physisorption well (Supplementary Discussion 5). Mechanistically, several effects can be invoked to explain the observed affinity of protons to interfaces. First, in hydronium ions, asymmetric charge distribution leads to an amphiphilic surfactant-like character \(^{25,26}\), which could lead to segregation due to the hydrophobic nature of the hBN interface. Second, the ionic nature of the insulating hBN crystal \(^{26}\) could also be responsible for electrostatic trapping of the positively charged hydronium ion. Third, as hydronium donates three hydrogen bonds to water, this leads to straining and disruption of the hydrogen-bonding network \(^{20}\). This effect is reduced at interfaces—at which the hydronium oxygen tends to point away from water \(^{21}\)—and could lead to trapping of the ion \(^{22,23}\). Note that although these simulations suggest that surface proton transport is characterized by purely bidimensional diffusion at the solid/water interface, measuring whether this is actually the case in our experiments would require detailed analysis of the statistical properties of the proton transit time between adjacent defects \(^{24}\). At this 100-nm scale, such measurements would require a temporal resolution of \(\Delta t \approx 1\,\mu\text{s}\), which is unfortunately unattainable with current state-of-the-art single-molecule tracking techniques \(^{25}\).

Conclusion
The combination of super-resolution microscopy and single-particle tracking on hBN defects allowed us to reveal proton trajectories between adjacent surface defects at the single-molecule scale. These observations establish that the solid/water interface provides a preferential pathway for proton transport, with excess protons remaining segregated at the surface, leading to the observed spatiotemporal correlations in the activation of nearby defects. The direct observation of this interfacial proton pathway has broad implications for charge transport in a range of fields and materials, and suggests that tuning of defect densities, binding affinities and illumination could allow the optimization and control of interfacial proton transport. Our experiments thus represent a promising platform for the investigation of proton transport at the single-molecule scale, opening up a number of avenues, for example, related to the interplay of flow or confinement with molecular charge transport at liquid/solid interfaces.

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Data availability
The data that support the findings of this study are available from the corresponding authors on reasonable request.

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Author contributions
J.C. and A.R. conceived and designed the experiments and J.C. performed the experiments with help from E.G. and A.A. J.C. analysed data and wrote the paper, with input from all authors. B.G. carried out simulations, with help from R.V. and M.-L.B, and K.W. and T.T. contributed materials. A.R. supervised the project. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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