monomers point their open ends either downwards (yellow) or upwards (magenta).

Two aspects of this arrangement are important for the success of the 2D polymerization: first, one of the two carbon–carbon triple bonds of each face is located above an anthracene ring of a neighbouring monomer (Fig. 1a, inset), positioning these groups appropriately for a subsequent light-induced cycloaddition reaction to fuse the layer into a covalently bonded sheet. Second, the layered crystal morphology derives from the monomer shape, and its alternate packing ensures that these close contacts are confined to independent layers, such that a true 2D periodic material is formed.

Irradiating single crystals of the monomer induced the 2D polymerization, as evidenced by the disappearance of the characteristic fluorescence of the anthracene moieties and by the insolubility of the photolysed crystals in good solvents for the monomer. Remarkably, these polymerized crystals could be exfoliated to individual layers by heating in solvent for extended periods (Fig. 1b). Atomic force microscopy indicated that the isolated sheets were uniformly 2.5 nm thick — consistent with the expected thickness of a monolayer — and some retained the lateral dimensions and hexagonal shape of the parent multilayer crystal. Furthermore, the 2D periodicity

of the multilayer crystal was preserved during exfoliation, as was evident from electron diffraction patterns recorded by transmission electron microscopy of few-layer samples. These results unambiguously demonstrate the success of this two-step polymerization–exfoliation approach.

This work will no doubt inspire further studies of the synthesis, characterization and properties of 2D polymers. It is crucial to demonstrate the generality of this strategy, particularly because topochemical reactions are often intolerant of small changes in the distances and relative orientations between reactive functional groups. Developing new classes of monomers capable of similar 2D polymerizations will be a challenge in crystal engineering, requiring both judicious design and pragmatic fine-tuning of the monomer structure. Computational methods for predicting molecular crystal structures are improving rapidly and might prove invaluable. Finally, it remains essential to develop methods that can unambiguously characterize all aspects of the chemical structure, long-range order, impurities and defects of 2D polymers, whether synthesized through existing or forthcoming approaches.

In the meantime, the present system offers in itself many possibilities for further inquiry. The mechanical properties of the free-standing sheets will be of great interest, as will methods that could fold,

stack and arrange them. As Sakamoto and colleagues point out, it might be possible to functionalize the 2D polymer, either through reactions at its remaining alkyne groups or by removing the aromatic cap of each monomer unit. In this way, the periodic structure of the 2D polymer might be used as a template to organize arbitrary functionality into precise, periodic arrays. Functionalization strategies able to differentiate the two sides of a 2D macromolecule represent a particularly intriguing way to make use of this type of architecture. In light of the unanswered questions and as-yet unexplored properties and applications of 2D polymers, we expect their synthesis and characterization to attract plenty of future attention. ❐

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References
1. Kissel, P. et al. Nature Chem. 4, 287–291 (2012).
2. Sakamoto, J., van Heijst, J., Lukin, O. & Schlüter, A. D. Angew. Chem. Int. Ed. 48, 1030–1069 (2009).
3. Côté, A. P. et al. Science 310, 1166–1170 (2005).
4. Berlanga, I. et al. Small 7, 1207–1211 (2011).
5. Colson, J. W. et al. Science 332, 228–231 (2011).
6. Dienstmaier, J. F. et al. ACS Nano 5, 9737–9745 (2011).
7. Zwaneveld, N. A. A. et al. J. Am. Chem. Soc. 130, 6678–6679 (2008).
8. Abel, M., Clair, S., Ourdjini, O., Mossoyan, M. & Porte, L. J. Am. Chem. Soc. 133, 1203–1205 (2011).

## ION DYNAMICS

Wired-up water

The splitting of water molecules into protons and hydroxide ions, and their recombination, occurs by proton transfer along hydrogen-bond wires. Now, first principle simulations of the recombination reaction reveal new atomic-scale details of the process showing that compression of the wire plays an important role.

David Chandler, Christoph Dellago and Phillip Geissler

Every chemistry student learns that all but one-in-a-billion molecules in pure liquid water are intact H_2O. The exceptions are generally hydroxide ions, OH^-, and hydrated protons, like the hydronium ion, H_3O^+. These charged species appear in pairs as the result of autoionization, the dissociation of a water molecule, and they disappear through recombination — a dynamic equilibrium without which pH would be irrelevant and much of aqueous chemistry would not occur. The molecular details of these processes are difficult to observe on account of their rarity: the half-life of an intact water molecule in liquid is about 10 hours, and

autoionization or recombination reactions, when they occur, are typically completed in around a picosecond over lengths less than 1 nm (ref. 1). Most of what is known about these processes at atomistic time and length scales has been learned from computer simulations, the most recent of which was described in the Proceedings of the National Academy of Sciences USA by Ali Hassanali, Michele Parrinello and co-workers[2]. This study exploits improved computing power and advances in electronic structure theory in its treatment of larger systems, enabling the collection of more data than previously allowed. The molecular picture is enriched as a result.

By imposing constraints on the solvation structures of hydronium and hydroxide ions, and on the distance between them, Hassanali, Parrinello and co-workers have prepared a large set of molecular configurations exemplifying microscopic charge separation. In each of these metastable or unstable arrangements, two ions are connected by a chain of hydrogen-bonded water molecules — essentially a wire through which the ions can rapidly recombine, requiring at most a small fluctuation to activate the recombination. Propagating short molecular dynamics trajectories from these charge-separated states, the authors generated the largest collection of recombination
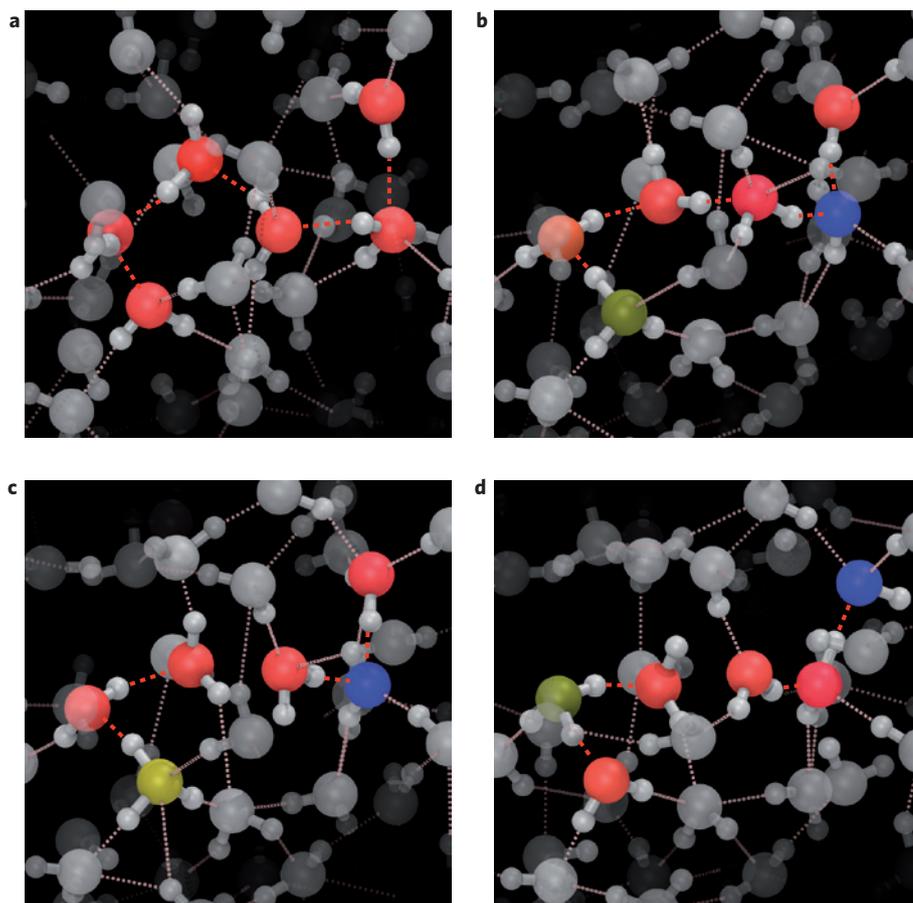
Figure 1 | Four snapshots from a rendering of a 0.15 ps trajectory exhibiting auto-ionization in water, **a** → **b** → **c** → **d** (or its reverse, ion recombination). The trajectory (a narrated video of which can be viewed online: http://www.youtube.com/watch?v=zeFSzt5x9uo) is typical of several examples of these rare events harvested from an ab initio molecular dynamics study[3]. Dashed lines indicate intermolecular hydrogen bonds. Those coloured red highlight the hydrogen bond wire along which protons move readily when an electrostatic potential destabilizes an O–H chemical bond. Red, blue and yellow oxygen atoms label H_2O, OH^- and H_3O^+, respectively. Grey molecules do not participate directly but rather influence charge transfer through electrostatic interactions that modulate the proton potential. The transition state for the process is crossed between time frames **b** and **c**, when the hydrogen-bond wire severs (or, in the reverse direction, mends), annihilating (or, in reverse, creating) a direct route for proton conduction.

trajectories so far, the details of which encode the mechanism of this fundamental process — and of its time-reversed counterpart, namely autoionization.

To emphasize the implications of the new results for our understanding of these processes, Fig. 1 shows a series of snapshots from a representative dissociation. This example of spontaneous charge separation was harvested in an earlier simulation study[3] by selecting from natural time evolution those trajectories that exhibit transitions between the neutral and the ionized state. Figure 1a exhibits the familiar, disordered and percolating hydrogen-bond network that is central to liquid water's many special properties. Dynamics over the ensuing 0.15 ps, which rearrange this network in subtle yet profound ways, arrive at the charge-separated state. This separation is spurred by a highly unusual fluctuation in proton potential (that is, the change in energy that results from moving protons along the hydrogen-bond wire in a concerted fashion). This fluctuation is large enough to destabilize an HO–H chemical bond and molecules that contribute to the fluctuating potential are many, both near and far. Hassanali, Parrinello and co-workers, have identified specific ways in which water molecules adjacent to the nascent hydronium and hydroxide ions modulate the proton potential, for example offering a larger-than-typical coordination number to the emerging centre of negative charge. As in Marcus's picture of electron transfer[4], however, more distant solvent molecules are also highly influential, contributing a collective electric field that can strongly bias proton conduction along the wire.

When such an extreme fluctuation in proton potential occurs, it does not last long, only 0.01 to 0.1 ps (ref. 5). This time interval is nonetheless long enough for the destabilized chemical bond to break and for the resulting ions to part by about 1 nm, as illustrated by the second pictured time frame Fig. 1b. The rapid separation is achieved through small amplitude motions of several protons, each molecule in the wire seizing a new proton from one hydrogen-bonded neighbour and relinquishing another proton to the next molecule along the wire. This collective translocation, driven by electrostatic forces from the solvent environment, is reminiscent of what is called the Grotthus mechanism for transport of an excess proton in liquid water[6,7]. But in the case of autoionization, the new arrangement of covalent bonds is not at this stage stable or even metastable. In fact, if nothing else happens, the proton translocation will proceed in reverse as the proton potential fluctuation disappears, leading back to the ion-free state.

The new study by Hassanali, Parrinello and co-workers reveals one way for this transient charge separation to become metastable. Specifically, they show that compression of the hydrogen-bond wire, shortening the distance between adjacent molecules by 5–10%, is prerequisite for recombination. In the context of autoionization this result suggests that metastable charge separation can be achieved by modest expansion of the wire. This local stability is marginal (resulting in a time to activated recombination of only about 0.5 ps), but it is sufficient to allow some separated ions to diffuse away from one another. The third pictured frame, Fig. 1c, illustrates an alternative source of metastability. Here, a coincidental rearrangement of the hydrogen-bond network severs the hydrogen-bond wire along which protons were conducted, blocking the original route for recombination. Different routes, along other connecting wires, are available, but they are less passable. As well as being longer and less direct, they are not compressed — these two mechanisms are thus not completely distinct, but act together to create long-lived charge-separated states.

This picture of an intricate interplay between electric fields and the hydrogen-bond network is drawn from theoretical calculations, and thus subject to the usual questions over model adopted, finite system sizes and statistics. For instance, further example trajectories are needed to clarify the relative efficaciousness of wire

expansion and wire breakage in rendering the charge-separated state metastable. When will these features be examined with natural experiments? The new[2] and earlier[3] simulations point to spectroscopic signals that could in principle be accessed, but finding these signals among all others presents a significant challenge. Given the results of the simulations, meeting this challenge will elucidate rich and multifaceted features of one of water's most fundamental processes.   ❐

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References
1. Eigen, M. & de Maeyer, L. *Proc. R. Soc. London A* **247,** 505–533 (1958).
2. Hassanali, A., Prakash, M. K., Eshet, H. & Parrinello, M. *Proc. Natl Acad. Sci. USA* **108,** 20410–20415 (2011).
3. Geissler, P. L., Dellago, C., Chandler, D., Hutter, J. & Parrinello, M. *Science* **291,** 2121–2124 (2001).
4. Marcus, R. A. & Sutin, N. *Biochim. Biophys. Acta* **811,** 265–322 (1985).
5. Hermenez, R., Fleming, G. R., Kumar, P. V. & Maroncelli, M. *Nature* **369,** 471–473 (1994).
6. Agmon, N. *Chem. Phys. Lett.* **244,** 456–462 (1995).
7. Voth, G. A. *Acc. Chem. Res.* **39,** 143–150 (2006).

POLYMER VESICLES

Autonomous propulsion

Polymer vesicles have been constructed that entrap platinum nanoparticles in their outer surface. These serve to break down a fuel of hydrogen peroxide, generating water and oxygen and in turn inducing a propulsive effect.
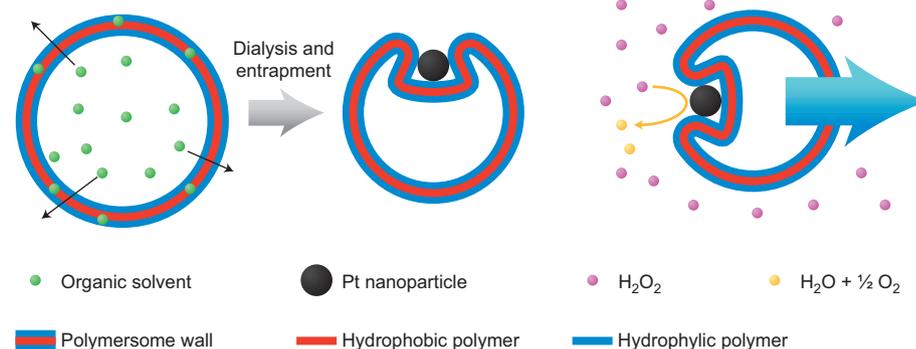
Jonathan Howse

As the quest for motility at the nanoscale continues unabated, a step — or a splash — forward for nanoscale swimming devices has been described in *Nature Chemistry* by Daniela Wilson, Roeland Nolte and Jan van Hest, who have used a solvent-driven shape-transformation phenomenon to construct a self-propelling system[1].

As Purcell mentioned in an early paper entitled 'Life at low Reynolds numbers', simply shrinking a technique or method that produces propulsion at the human scale will not necessarily give one that works at the nanoscale[2]. For nanoscale objects in water, viscous forces dominate, and water actually appears as a thick viscous liquid — an oversight in Hollywood movies such as Fantastic Voyage and Innerspace.

What is most important for objects to be able to swim at small length scales in this thick treacle-like environment is some degree of asymmetry, be it physical or temporal. For example, consider the motion of a theoretical miniaturized scallop, with its single hinge: opening its shell will propel the scallop in one direction, but closing it will simply result in equivalent propulsion in the opposite direction — back to its starting point. A single hinge can only demonstrate reciprocal motion, as opposed to generating propulsion. Successful non-reciprocal motion is found for flagella and cilia, for example, or as in Purcell's hypothesized three-link swimmer that consists of three straight arms connected in series by — most importantly — two hinges.

A physical analogue of the non-reciprocal motion is a physical asymmetry in the nanoscale object, so that a propulsive effect

Organic solvent   Pt nanoparticle   H₂O₂   H₂O + ½ O₂

Polymersome wall   Hydrophobic polymer   Hydrophylic polymer

Figure 1 | Formation of the platinum-loaded stomatocyte polymersomes. **a,** Polymersomes are assembled in a mixture of organic solvents (dioxane and THF) in the presence of water. **b,** The addition of platinum nanoparticles during dialysis results in a polymersome with a smaller internal volume yet with constant surface area, which collapses in upon itself and physically traps the nanoparticles. **c,** Exposure to a fuel of hydrogen peroxide allows the exposed platinum to catalyse the breakdown of hydrogen peroxide to water and oxygen, in turn generating propulsion.

is created on only part of the nanoscale device. The approach was first demonstrated by Whitesides[3] with the motility of millimetre-sized polydimethylsiloxane (PDMS) plates decorated with small pieces of platinum-coated glass. These early studies were an elegant progression of the relatively large 'camphor boats' (small centimetre-size boats loaded at one end with camphor) familiar to many[4]. An asymmetric coating of platinum catalyses the decomposition of hydrogen peroxide (which thus serves as molecular fuel) into water and oxygen, releasing oxygen bubbles from only one area of the PDMS plate, in turn pushing the particle along. This approach of an asymmetric catalyst, be it part of a bimetallic system[5] or a coating on a non-conducting

colloid[6], has been used to produce autonomous motion of devices down to sub-micrometre length scales[7].

Now, Wilson, Nolte and van Hest have adopted a different approach, which allows for the generation of the required physical asymmetry in initially spherical polymer vesicles (polymersomes), and so combines the propulsion aspect with the drug-carrier capabilities and functionalities already commonly found in polymersomes. These polymeric analogues of liposomes are made from amphiphilic diblock copolymers (Fig. 1a) and offer greater mechanical stability, functionalization and decreased diffusion through the membrane than their lipidic counterparts — which is why they can be seen as ideal drug-delivery devices[8].