Nanoscale

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Nanoscale*, 2017, **9**, 6953

Received 16th November 2016,
Accepted 10th April 2017

DOI: 10.1039/c6nr08944e

rsc.li/nanoscale

An optically-gated AuNP–DNA protonic transistor†

Songming Peng, *‡[a] Amit Lal,[b] Dan Luo[a] and Yuerui Lu*§[b]

Bio-interface transistors, which manipulate the transportation of ions (*i.e.* protons), play an important role in bridging physical devices with biological functionalities, because electrical signals are carried by ions/protons in biological systems. All available ionic transistors use electrostatic gates to tune the ionic carrier density, which requires complicated interconnect wires. In contrast, an optical gate, which offers the advantages of remote control as well as multiple light wavelength selections, has never been explored for ionic devices. Here, we demonstrate a light-gated protonic transistor fabricated from an Au nanoparticle and DNA (AuNP–DNA) hybrid membrane. The device can be turned on and off completely by using light, with a high on/off current ratio of up to 2 orders of magnitude. Moreover, the device only responds to specific light wavelengths due to the plasmonic effect from the AuNPs, which enables the capability of wavelength selectivity. Our results open up new avenues for exploring remotely controlled ionic circuits, *in vivo* protonic switches, and other biomedical applications.

The electronic transistor has been playing a key role in modern electronics. In general, signals are carried by electrons in these solid state devices. In contrast, in biological systems, electrical signals are conducted through ions/protons instead of electrons.[1] Numerous examples include: V-ATPase-driven proton pumps that acidify intracellular organelles,[2] HVCN1 voltage-gated proton channels for proton transport into phagosomes,[3] light induced proton transport through a cell membrane to catalyze ATP synthesis[4–6] and so on. Thus, in order to interface with biological systems, spatially and temporally controlled delivery of ions/protons is desirable.[7–10] Towards this end, ionic transistors have been recently developed to control ion transport,[11–15] which have been successfully utilized in biomedical applications including regulating Ca^{2+} signaling in neuronal cells,[16] modulating nerve impulses[17] and *in vivo* recordings of brain activity.[18] Currently, all of these ion transistors use a voltage gate to tune the ionic carrier density. On the other hand, optical signals offer the advantages of remote control and wavelength selectivity.[19–21] Therefore, a new type of protonic transistor made of smart materials sensitive to light will allow us to use light to remotely control the propagation of electrical signals in biological systems.

Here, we demonstrate, for the first time, an optically-gated protonic transistor, using a light-sensitive smart material, an AuNP–DNA hybrid membrane. AuNPs possess numerous unique optical properties.[22,23] For instance, the absorption peak of an AuNP can be tuned precisely from visible to near-infrared (near-IR) regions by changing the size and shape of the AuNP.[23–25] In addition, an AuNP transforms the photons absorbed to heat efficiently (efficiency close to 100%).[26] On the other hand, DNA that encodes genetic information is a naturally occurring polyelectrolyte. The phosphate groups on the DNA backbone have an ionization pK_a as low as 1.5,[27,28] making DNA an effective proton donor and carrier. The ionized proton can be conducted through a network of hydrogen bonded water molecule chains[12,29] that act as proton conducting channels, which is formed along the DNA backbone.[30,31] In addition, DNA is easily modified with a variety of different chemical groups, including thiol groups, making attachment to the surface of the AuNPs convenient. Moreover, previous reports have indicated that DNA or DNA–metal complexes can mediate charge transport.[32,33] Whether DNA can also be utilized to mediate proton transfer has not been explored.

Our device utilizes each of these unique properties of AuNPs and DNA (Fig. 1a and b). The current flow comes from transport of the protons in the membrane, which can be efficiently modulated by remote light illumination. The photons, mainly absorbed by the AuNPs, can effectively tune

[a]*Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY, USA. E-mail: songming@caltech.edu*
[b]*School of Electrical and Computer Engineering, Cornell University, Ithaca, NY, USA. E-mail: yuerui.lu@anu.edu.au*

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6nr08944e

‡Current address: Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, USA.
§Current address: Research School of Engineering, College of Engineering and Computer Science, The Australia National University, Canberra, 2601, Australia.

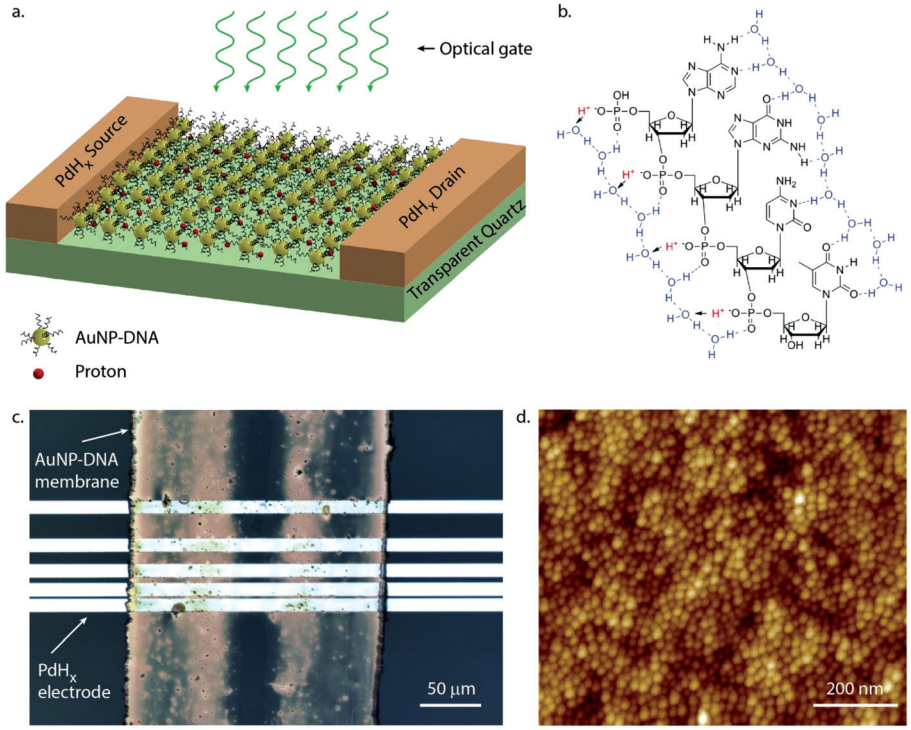

Fig. 1 Schematic illustration and characterization of the AuNP–DNA protonic transistor. (a) A PdH_x source and drain were patterned on top of the transparent quartz. The AuNP–DNA membrane was formed between the source and drain. Green light (532 nm) was used as the optical gate to control the on and off states of the device. (b) Protons were ionized from the phosphate group of the DNA and conducted through the network of hydrogen bonded water molecule chains formed along the DNA molecules. (c) Microscopy image of the AuNP–DNA protonic transistor (device was placed on top of silicon wafer to enhance the contrast). (d) Atomic force microscopy (AFM) image of the AuNP–DNA membrane.

proton density in the membrane, by changing the hydration and ionization level of DNA molecules. More interestingly, the device only responds to specific light wavelengths because of the plasmonic effect from the AuNPs, which offers wavelength selectivity in this optically-gated protonic transistor. Since AuNPs can be easily tuned to absorb near-IR light that can penetrate tissues efficiently,[20] our device has the potential to be used in biological systems for *in vivo* sensing and actuation applications.

Palladium (Pd) electrode pairs, with various channel gaps, were patterned on a transparent quartz substrate, using conventional optical lithography and metal deposition processes. When exposed to hydrogen, the palladium electrode reacted with hydrogen to form PdH_x, which served as the proton source.[34–36] DNA functionalized AuNPs were carefully dropped on the device and dried in air to form an AuNP–DNA membrane (Fig. 1c), bridging the PdH_x electrodes. The surface morphology of the AuNP–DNA membrane was characterized by atomic force microscopy (AFM). The AFM image indicates that the AuNPs were well separated from each other without forming AuNP aggregates (Fig. 1d). The good separation was due to the DNA corona layer on the AuNP. The DNA corona served as the buffer region to prevent AuNP aggregation and inhibit electrons conduction between the AuNPs.[37]

The PdH_x electrodes are critical for our protonic transistors as they serve as both the source and the receiver for photon transport.[38] The function of PdH_x was confirmed by using gold electrodes and Pd electrodes as controls, respectively. For devices with similar dimensions, minimal protonic current was detected for both gold and Pd electrode devices (Fig. 2a and S1a & Table S1†). On the other hand, the current increased 133-fold when the electrodes were converted from Pd to PdH_x (Fig. 2a & Table S1†). These results suggested that the PdH_x indeed functioned as the proton source and the current was derived from the proton conduction, rather than electron conduction. In addition, a minimum protonic current change was observed when replacing the AuNP–DNA membrane with the AuNP–PEG membrane, further indicating that DNA is an efficient proton donor and carrier (Fig. S1b†). Moreover, the AuNP–DNA film demonstrated a linear relationship between the resistance and channel length of the device (Fig. 2b). The measured data can be fitted by the following equation:

$$R = A \times L + B$$

where R is the total resistance, L is the channel length, A is the coefficient for the channel resistance of protons in the AuNP–DNA membrane, and B is the contact resistance. Through fitting, the values of A and B for devices with Pd (PdH_x) electrodes were found to be 1.3 (0.0084) and 4.5 (0.0381) GΩ, respectively. The channel resistance and contact resistance for Pd electrodes were found to be around 155-fold and 118-fold

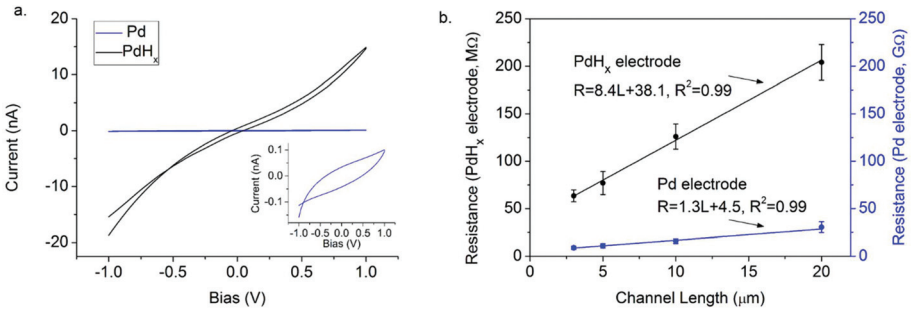

Fig. 2 Protonic conductivities of the devices with different electrode contacts. (a) Measured protonic current as a function of the voltage bias for the devices with Pd (blue line and insert) and PdH_x (black line) electrodes. (The channel length was fixed at 3 μm.). (b) Measured resistance as a function of the channel length for devices with Pd and PdH_x electrode contacts.

larger than those for the PdH_x electrode, which further confirms the superior function of the PdH_x for proton transport.

While DNA is an excellent source and carrier for proton transport, DNA thin films have very weak optical absorption (Fig. 3a). The coupling of AuNPs with DNA significantly enhances the optical response by orders of magnitude (Fig. 3a). In particular, the plasmonic effect from these AuNPs[23] offers a sharp absorption peak at ~560 nm. We observed a small shift of the absorption peak wavelength between dried AuNP–DNA films (562 nm) and AuNP–DNA solution (525 nm, Fig. S2†), which could be due to the plasmonic coupling of dried AuNPs in close proximity.[39]

This AuNP–DNA hybrid membrane is a perfect smart material for optically-gated protonic transistors, since it possesses both a high optical response and high proton conductivity. We found that our protonic transistor was very sensitive to the power density of illumination light (wavelength 532 nm). At a relatively low illumination power density of 20 mW mm^{-2}, the device was fully turned off, with a current on/off ratio up to 27 (Fig. 3b, black circles and yellow circles). This on/off ratio is 9 times higher than that of the first protonic transistor with electrostatic gating.[12] In addition, the current was readily tuned by using different light intensities (Fig. 3b, red, blue, cyan and pink circles). More interestingly,

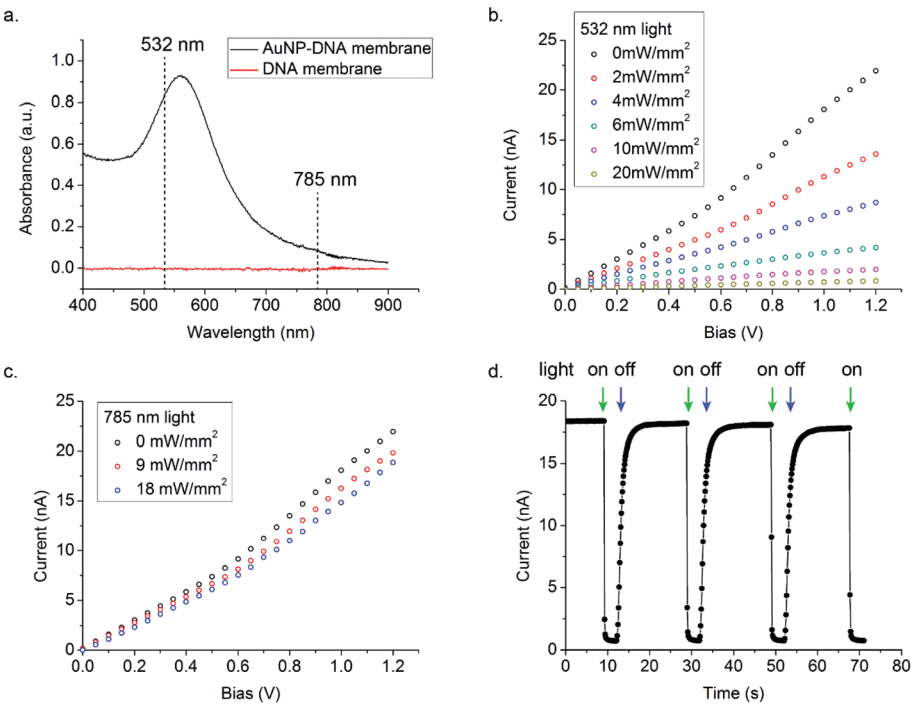

Fig. 3 Characterization of the optically gated AuNP–DNA protonic transistor. (a) Measured absorption spectra curves of the AuNP–DNA and DNA membranes on quartz. (b and c) Measured *current vs. bias* characteristics of the protonic transistor under different illumination light intensities at wavelengths of 532 nm (b) and 785 nm (c), respectively. (d) Measured device real-time current response curve under intermittent light illumination (20 mW mm^{-2}, bias was fixed at 1 V) at a wavelength of 532 nm.

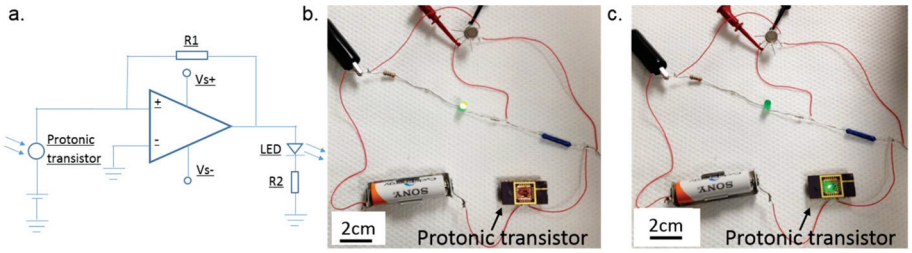

Fig. 4 The demonstration of a light switch using our optically gated protonic transistor. (a) Schematic drawing of the electrical circuit. (b) Light emitting diode (LED) was on when the illumination light was off. (c) LED was turned off when the illumination light was shone onto the device.

the device only responded to specific wavelengths. When 785 nm light was used as the illumination source, minimal effects on the protonic conductivity were observed, demonstrating the specific wavelength selectivity of the device (Fig. 3c). The wavelength selectivity is due to the fact that AuNPs effectively absorb light at 532 nm, while having minimum absorption at 785 nm (Fig. 3a). AuNPs transform the absorbed photons to heat with an efficiency close to 100%,[26] resulting in a drastic protonic conductivity change in 532 nm light, not in 785 nm light. To measure the device responsiveness under the illumination of 532 nm light, a real time protonic current was monitored. The results indicated that the current dropped close to zero within 0.3 seconds when the light was switched on (Fig. 3d, green arrows), and recovered within 4 seconds after the light was switched off (Fig. 3d, blue arrows). Our devices possess fast optical responses, simple device fabrication processes, and high repeatability (Fig. S3†), which will enable numerous potential applications.

The mechanism for the light induced protonic conductivity change was then investigated. Since AuNPs efficiently converted the absorbed light to local heat,[26] and since DNA hydration was essential for DNA ionization to generate protons, we hypothesized that the light induced local AuNP temperature change produced the conductivity change. To test this hypothesis, we changed the temperature both globally and locally. When the global temperature was increased, the protonic current also increased (Fig. S4a†). However, when the device was only heated from the bottom, the protonic current dropped dramatically (Fig. S4b†). Since the device was kept in an 80% humidity chamber, when increasing the global temperature, more water molecules tended to absorb onto the DNA, which led to increased DNA ionization, proton transfer and proton current. However, when only the local device temperature was changed, while the global temperature was maintained the same, it caused the water molecules to quickly dissociate from the phosphate and DNA bases, which led to decreased DNA ionization, proton transfer and proton current. These results indicated that the local temperature change was responsible for the current change.

Numerous applications can be envisioned using a light gated protonic device. As a simple demonstration, we used light to turn off light. The protonic device was packaged, and then connected with an amplifier and a light-emitting diode (Fig. 4a). When the illumination light was off, the current going through the device was amplified and the diode was on (Fig. 4b). On the other hand, when the illumination light was remotely shone onto the device, the current going through the device was dropped by 27-fold and the diode was successfully shut off (Fig. 4c).

In conclusion, we have demonstrated an optically-gated protonic transistor based on an AuNP–DNA membrane. Interestingly, Gorodetsky and coworkers[40] have demonstrated a photochemical doped protonic transistor, where upon light illumination, more protons would be released from a small proton donor (8-hydroxypyrene-1,3,6-trisulfonic acid), resulting in an increased proton conductivity. On the other hand, the protonic current of our device was well tuned down upon remote light illumination. In addition, the device only responded to specific light wavelengths, which was enabled by the plasmonic effect of the AuNP. By designing AuNPs with different light absorptions,[23] our device could be potentially used in light based computing. Moreover, by using infra-red absorption AuNPs, our device can be designed for remotely controlled protonic switches and other bio-interfacial applications.

Methods

DNA functionalized AuNP preparation

Thiolated ssDNA (DNA sequence 5′ SH-TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT, IDT DNA) was reduced by TCEP (Sigma) to activate the thiol group. The activated ssDNA was purified using the Bio-spin column (Biorad) and then added to the solution of 15 nm AuNPs (Ted Pella). Sodium chloride solution (final concentration 500 mM) was added to the AuNPs to minimize the charge repelling effect between DNAs to maximize DNA coating on the AuNPs. DNA functionalized AuNPs were washed thoroughly with milli-Q water by repeated centrifugation to remove free salt ions in solution.

Device fabrication and characterization

Metal electrodes (Au and Pd) were patterned using conventional optical lithography, metal evaporation and lift off processes. DNA functionalized AuNPs were carefully dropped on the

device and dried in air to form an AuNP–DNA membrane. The absorption spectrum of the AuNP–DNA membrane was measured by using a UV-Vis-NIR spectrometer (Shimadzu). The morphology of the AuNP–DNA membrane was imaged by using an AFM-3100. PdH_x electrodes were obtained by soaking Pd electrodes in a sealed measuring/humidity chamber with H_2 (1 atm) overnight. Laser diodes (532 nm and 785 nm, Thorlabs) were used to illuminate the protonic transistors, for gating effect characterization. Electrical measurements were carried out using the Keithley 4200 station (Keithley) at room temperature and 80% relative humidity in a humidity chamber, with samples located in a probing station.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

This work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC program (DMR-1120296).

References

1 J. Magee, D. Hoffman, C. Colbert and D. Johnston, Electrical and calcium signaling in dendrites of hippocampal pyramidal neurons, *Annu. Rev. Physiol.*, 1998, **60**, 327–346.
2 M. Forgac, Vacuolar ATPases: rotary proton pumps in physiology and pathophysiology, *Nat. Rev. Mol. Cell Biol.*, 2007, **8**, 917–929.
3 D. Morgan, *et al.*, Voltage-gated proton channels maintain pH in human neutrophils during phagocytosis, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 18022–18027.
4 J. W. Ho and E. S. M. Po, Light-induced proton transport through chloroplast membranes, *Biochem. Educ.*, 1996, **24**, 179–180.
5 S. Subramaniam and R. Henderson, Molecular mechanism of vectorial proton translocation by bacteriorhodopsin, *Nature*, 2000, **406**, 653–657.
6 T. J. M. Luo, R. Soong, E. Lan, B. Dunn and C. Montemagno, Photo-induced proton gradients and ATP biosynthesis produced by vesicles encapsulated in a silica matrix, *Nat. Mater.*, 2005, **4**, 220–224.
7 M. Irimia-Vladu, E. D. Glowacki, G. Voss, S. Bauer and N. S. Sariciftci, Green and biodegradable electronics, *Mater. Today*, 2012, **15**, 340–346.
8 M. Irimia-Vladu, "Green" electronics: biodegradable and biocompatible materials and devices for sustainable future, *Chem. Soc. Rev.*, 2014, **43**, 588–610.
9 C. Z. Liao, *et al.*, Flexible Organic Electronics in Biology: Materials and Devices, *Adv. Mater.*, 2015, **27**, 7493–7527.
10 G. Tarabella, *et al.*, New opportunities for organic electronics and bioelectronics: ions in action, *Chem. Sci.*, 2013, **4**, 1395–1409.
11 K. Tybrandt, K. C. Larsson, A. Richter-Dahlfors and M. Berggren, Ion bipolar junction transistors, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 9929–9932.
12 C. Zhong, *et al.*, A polysaccharide bioprotonic field-effect transistor, *Nat. Commun.*, 2011, **2**, 476.
13 K. Tybrandt, R. Forchheimer and M. Berggren, Logic gates based on ion transistors, *Nat. Commun.*, 2012, **3**, 871.
14 M. Magliulo, *et al.*, Electrolyte-Gated Organic Field-Effect Transistor Sensors Based on Supported Biotinylated Phospholipid Bilayer, *Adv. Mater.*, 2013, **25**, 2090–2094.
15 G. Sun, S. Senapati and H. C. Chang, High-flux ionic diodes, ionic transistors and ionic amplifiers based on external ion concentration polarization by an ion exchange membrane: a new scalable ionic circuit platform, *Lab Chip*, 2016, **16**, 1171–1177.
16 J. Isaksson, *et al.*, Electronic control of Ca^{2+} signalling in neuronal cells using an organic electronic ion pump, *Nat. Mater.*, 2007, **6**, 673–679.
17 Y. A. Song, *et al.*, Electrochemical activation and inhibition of neuromuscular systems through modulation of ion concentrations with ion-selective membranes, *Nat. Mater.*, 2011, **10**, 980–986.
18 D. Khodagholy, *et al.*, In vivo recordings of brain activity using organic transistors, *Nat. Commun.*, 2013, **4**, 1575.
19 L. V. Wang and J. Yao, A practical guide to photoacoustic tomography in the life sciences, *Nat. Meth.*, 2016, **13**, 627–638.
20 T.-M. Liu, J. Conde, T. Lipinski, A. Bednarkiewicz and C.-C. Huang, Revisiting the classification of NIR-absorbing/emitting nanomaterials for in vivo bioapplications, *NPG Asia Mater.*, 2016, **8**, e295.
21 D. Tischer and O. D. Weiner, Illuminating cell signalling with optogenetic tools, *Nat. Rev. Mol. Cell Biol.*, 2014, **15**, 551–558.
22 Z. Nie, A. Petukhova and E. Kumacheva, Properties and emerging applications of self-assembled structures made from inorganic nanoparticles, *Nat. Nano*, 2010, **5**, 15–25.
23 S. Eustis and M. A. El-Sayed, Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes, *Chem. Soc. Rev.*, 2006, **35**, 209–217.
24 C. J. Murphy, *et al.*, Anisotropic metal nanoparticles: Synthesis, assembly, and optical applications, *J. Phys. Chem. B*, 2005, **109**, 13857–13870.
25 M. R. Jones, K. D. Osberg, R. J. Macfarlane, M. R. Langille and C. A. Mirkin, Templated Techniques for the Synthesis and Assembly of Plasmonic Nanostructures, *Chem. Rev.*, 2011, **111**, 3736–3827.
26 H. H. Richardson, M. T. Carlson, P. J. Tandler, P. Hernandez and A. O. Govorov, Experimental and Theoretical Studies of Light-to-Heat Conversion and

Collective Heating Effects in Metal Nanoparticle Solutions, *Nano Lett.*, 2009, **9**, 1139–1146.

27 W. D. Kumler and J. J. Eiler, The acid strength of mono and diesters of phosphoric acid. The n-alkyl esters from methyl to butyl, the esters of biological importance, and the natural guanidine phosphoric acids, *J. Am. Chem. Soc.*, 1943, **65**, 2355–2361.

28 S. I. Chamberlin, E. J. Merino and K. M. Weeks, Catalysis of amide synthesis by RNA phosphodiester and hydroxyl groups, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 14688–14693.

29 J. F. Nagle, M. Mille and H. J. Morowitz, Theory of Hydrogen-Bonded Chains in Bioenergetics, *J. Chem. Phys.*, 1980, **72**, 3959–3971.

30 B. Schneider, D. Cohen and H. M. Berman, Hydration of DNA Bases - Analysis of Crystallographic Data, *Biopolymers*, 1992, **32**, 725–750.

31 B. Schneider, K. Patel and H. M. Berman, Hydration of the phosphate group in double-helical DNA, *Biophys. J.*, 1998, **75**, 2422–2434.

32 A. A. Gorodetsky, M. C. Buzzeo and J. K. Barton, DNA-Mediated Electrochemistry, *Bioconjugate Chem.*, 2008, **19**, 2285–2296.

33 J. K. Barton, E. D. Olmon and P. A. Sontz, Metal complexes for DNA-mediated charge transport, *Coord. Chem. Rev.*, 2011, **255**, 619–634.

34 H. Morgan, R. Pethig and G. T. Stevens, A Proton-Injecting Technique for the Measurement of Hydration-Dependent Protonic Conductivity, *J. Phys. E: Sci. Instrum.*, 1986, **19**, 80–82.

35 D. D. Ordinario, L. Phan, J. M. Jocson, T. Nguyen and A. A. Gorodetsky, Protonic transistors from thin reflectin films, *APL Mater.*, 2015, **3**, 014907.

36 Y. X. Deng, *et al.*, H+-type and OH–type biological protonic semiconductors and complementary devices, *Sci. Rep.*, 2013, **3**, 2481.

37 W. L. Cheng, N. Y. Park, M. T. Walter, M. R. Hartman and D. Luo, Nanopatterning self-assembled nanoparticle superlattices by moulding microdroplets, *Nat. Nanotechnol.*, 2008, **3**, 682–690.

38 T. B. Flanagan and W. A. Oates, The Palladium-Hydrogen System, *Annu. Rev. Mater. Sci.*, 1991, **21**, 269–304.

39 W. L. Cheng, *et al.*, Free-standing nanoparticle superlattice sheets controlled by DNA, *Nat. Mater.*, 2009, **8**, 519–525.

40 D. D. Ordinario, *et al.*, Photochemical Doping of Protonic Transistors from a Cephalopod Protein, *Chem. Mater.*, 2016, **28**, 3703–3710.

