

Small molecule crystals with 1D water wires modulate electronic properties of surface water networks

Nina Saraei^a, Alexander J. Gupta^b, Oleksandr Hietsoi^{a,c}, Brian C. Frye^a,
Dillon T. Hofsommer^a, Gamini Sumanasekera^d, Gautam Gupta^b, Mark S. Mashuta^a,
Robert M. Buchanan^{a,*}, Craig A. Grapperhaus^{a,*}

^a Department of Chemistry, University of Louisville, Louisville, KY, 40292, USA

^b Department of Chemical Engineering, University of Louisville, Louisville, KY, 40292, USA

^c Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN, 37132, USA

^d Department of Physics and Astronomy, University of Louisville, Louisville, KY, 40292, USA

ARTICLE INFO

Article history:

Received 3 August 2020

Revised 26 October 2020

Accepted 24 November 2020

Keywords:

Surface conductivity

Electronic properties

Proton mobility

Water wires

Humidity sensor

ABSTRACT

This study evaluates the effect of water vapor pressure on the surface conductivity of a hydrated small molecule crystal under dry and wet conditions. The crystal contains a discrete metal complex with waters of hydration in structural positions and in 1D water wires. Under dry conditions, the surface of the hydrated crystal behaves as a near ideal capacitor. Under wet conditions, the waters of hydration serve as a template to assemble surface water networks by organization of water from the environment. The surface water provides pathways for charge transfer attributed to proton mobility that increases conductivity by > 3 orders in magnitude. Modulation between wet and dry conditions tunes the conductivity of the crystal surface via a two-step process, which has been evaluated kinetically as a function of the water vapor pressure.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Water is a remarkable molecule and its complex molecular behavior continues to generate intense scientific interest [1,2]. It plays a crucial role in biochemical processes [3–6] and the development of biomimetic artificial water channels have led to a greater understanding of the hydrodynamics of water in confined environments [7–10]. There are also numerous examples of water clusters of various shapes and sizes in different host matrix environments [11–16]. The pores and channels generally are lined with organic moieties containing carbonyl, amine, or hydroxyl groups that facilitate hydrogen bonding. Within these channels, water serves as a conduit for proton mobility along water wires according to the Grotthuss [17–19] and vehicle mechanisms [20]. Dehydration of the channel may be irreversible due to collapse of the structure or reversible via single crystal to single crystal structural transformations with considerable changes in the material properties between the hydrated and dehydrated states [21,22]. Recently, materials that undergo reversible structural transformation upon

hydration have been employed to study proton propagation relevant to proton-exchange membranes or humidity sensors. Several metal-organic framework (MOF) materials demonstrate high proton conductivity under humid (94–98%) conditions attributed to an extended hydrogen-bonding network within the material upon hydration [23–28]. One of the MOFs demonstrated potential applicability as a humidity sensor with a five orders of magnitude enhancement in conductivity when the relative humidity was increased from 40% to 95% [23]. Similarly, an iron based perovskite $\text{BaFeO}_{2.5-x}(\text{OH})_{2x}$ [29], an open-framework chalcogenide [30], and a porous organic molecular material [31] demonstrated reversible increases in conductivity upon adsorption of water into the lattice. Proton conductivity has also been observed in coordination polymers through extended water networks between 2D layers [32] and in single crystals of coordination polymers [33]. Further evaluation identified two mechanisms for the enhanced conductivity at higher humidity of the single crystal with a lower barrier route attributed to a proton hopping mechanism through the interior of the crystal and a higher barrier route associated with mass transport on the crystal surface [33].

Water also displays unique properties when confined to a 2D surface. For instance, the structure and dynamics of water at mineral surfaces varies significantly from bulk water due to surface-

* Corresponding author.

E-mail addresses: robert.buchanan@louisville.edu (R.M. Buchanan), craig.grapperhaus@louisville.edu (C.A. Grapperhaus).

specific hydrogen bonding, orientation, and ordering that is dependent on the hydrophilicity/hydrophobicity of the mineral surface [34]. Relative to bulk water, water confined into 2D layers participate in fewer hydrogen bonds per molecule with decreased H-bond life times and increased lateral diffusion [35]. Charge propagation through water on surfaces has largely been attributed to the presence of Zundel [36] and Eigen [37] ions or small water clusters [38] that influence surface electrical and ionic conduction via an electrochemically mediated charge transfer process. The pH of the ambient environment dictates the direction to or from the host matrix of the charge transfer. The organization of water on surfaces has also been exploited to enhance proton conductivity. Unlike the materials that undergo structural changes upon adsorption of water into the lattice, the surface adsorption of water relies on interactions with surface features to organize water networks. For example, oxygen deficiencies in a 2D $\text{Ti}_3\text{C}_2/\text{TiO}_2$ composite provides a surface capable of detecting water over a wide relative humidity range (9–97%) through changes in conductivity. Ultrafast humidity detection was obtained using 2D graphene oxides that used changes in impedance to detect changes in humidity near the sensor associated with activities such as speaking, breathing, or whistling [39].

Herein, we report a system that undergoes dramatic changes in conductivity as a function of water vapor pressure associated with the adsorption of water on the surface of small molecule single crystals. To our knowledge, this is the first example of a discrete, small molecule metal complex that demonstrates this property. The system consists of 1D water chains confined in channels formed by 1D π -stacked metal complexes that are linked with structural waters of hydration. The waters of hydration serve as imprinted elements for the adsorption/desorption of an organized water network on the surface of the crystal that are responsible for the changes in surface conductivity under dry and wet conditions. This is in contrast to other materials that undergo changes in conductivity through the material associated with hydration/dehydration of the lattice. Interestingly, structurally similar complexes with blocked edges (with epoxy) or containing discontinuous water chains do not display this behavior. These systems demonstrate the potential to design small molecule complexes with tailored functional groups to imprint sites on crystalline surfaces to mediate surface electronic properties through the adsorption of water or other small molecules.

2. Results and discussion

Recently, we reported the synthesis and characterization of N,N' -(ethane-1,2-diyl)bis(1-methyl-1H-imidazole-2-carboxamido) nickel(II) hydrate ($\text{NiL}\cdot\text{H}_2\text{O}$) (Fig. 1A) and its isostructural Cu(II) derivative, which show extended hydrogen bonding (HB) network consisting of 1D water wires (Fig. 1B) in the crystal structure [40]. Crystals of $\text{NiL}\cdot\text{H}_2\text{O}$ contain two crystallographically distinct NiL equivalents and four unique water sites; three of which are full occupancy and one with partial occupancy. Preliminary evaluation of the electrical properties of $\text{NiL}\cdot\text{H}_2\text{O}$ suggested the presence of a *wet domain* associated with charge transfer through the HB water network and a *dry domain* associated with a water-deficient charge transfer pathway [40]. To further probe the electrochemical properties of this system, a single plate-shaped crystal of $\text{NiL}\cdot\text{H}_2\text{O}$ was mounted on a measurement chip that was loaded into a two-probe resistance measurement system that allowed for precise control of the water vapor pressure. For as-isolated crystals, a constant current of 52 ± 3 nA (at a constant applied voltage) was maintained for 7–8 min under initial, ambient conditions. Dry conditions were obtained by applying vacuum to reduce the $P_{\text{H}_2\text{O}}$ to 8 torr resulting in a rapid decrease in current (at the same applied voltage) to a steady value of 8 ± 3 pA. Then, wet

conditions were established by introducing water vapor until the $P_{\text{H}_2\text{O}}$ reached 17 torr. Within several minutes a constant current of 52 ± 3 nA was re-established. Multiple cycles of dry and wet conditions were performed with reproducible results (Fig. 1C). The behavior is consistent with modulation of surface conductivity through the formation and disruption of organized water networks. The phenomenon is reproducible using different crystals of $\text{NiL}\cdot\text{H}_2\text{O}$, although the value of current under wet conditions is dependent on the crystal size and electrode placement.

The electrical properties of the mounted crystal were evaluated by electrochemical impedance spectroscopy (EIS) under dry ($P_{\text{H}_2\text{O}} = 8$ torr) (Fig. 1D) and wet ($P_{\text{H}_2\text{O}} = 17$ torr) (Fig. 1E) conditions (see Supporting Information for further details). Under dry conditions, the crystal behaves as a near ideal capacitor (Fig. S2 and Table S1) with a small measured capacitance of 0.148 ± 0.02 nF attributed to the charging of the bulk crystal, which has a low density of dielectric. Under wet conditions, surface adsorbed water provides a path for charge transfer between the electrodes (Fig. S3 and Table S2). At high frequency, the alternating voltage signal builds charge across the crystal with a capacitance (CPE_1) of 0.092 ± 0.02 nF, similar to that of the dry crystal. As the frequency decreases, charge is transferred between the electrical contacts and water agglomerated around the contacts with an associated resistance (R_1) of 0.198 ± 0.002 M Ω and through the highly resistive surface water network, $R_2 = 1.116 \pm 0.006$ M Ω . As the frequency decreases further, capacitive charging occurs across the surface water, $\text{CPE}_2 = 1.0 \pm 0.7$ μF .

To evaluate if the conductivity is on the crystal surface or through the crystal, the AC resistance and EIS studies were repeated with the probes attached on opposing crystal faces. The conductivity under dry conditions, 18 ± 7 pA, is similar to the prior measurements. Under wet conditions, there is an increase in conductivity to 0.52 ± 0.01 nA (Fig. S4). However, the increase in current is two orders of magnitude lower than measurements with the probes on the same crystal face. Evaluation of the electrical properties of the crystal by EIS under dry conditions show a similar capacitance, 0.170 ± 0.003 nF, as when the probes were on the same crystal face consistent with its assignment to charging of the bulk crystal (Fig. S5, Table S3). However, when the crystal is hydrated only one time constant is apparent in the impedance spectrum (Fig. S6, Table S4). In this case, the measured charge transfer resistance, 26.7 ± 0.9 M Ω , is an order of magnitude greater than the resistance measured for charge propagation through the surface water film when the contacts are on the same side of the crystal. Capacitive charging of surface water is not observed in this case because of: (i) increased distance between the probes (larger effective dielectric thickness) and, more importantly, (ii) smaller effective dielectric cross sectional area as charge must build across the bottleneck region on the edges of the crystal where surface water coverage is sparse owing to the relative absence of anchoring structural water. These phenomena effectively reduce capacitance across the surface water film to zero, eliminating CPE_2 and combining R_1 and R_2 into a single parameter R (Fig. S7). This parameter represents the combined effect of electrical contact resistance between the probes and surface water film and the charge transfer resistance, which is greatly increased due to a charge propagation bottleneck along the edges of the crystal. As with the same side probe placement measurements, charge propagation and/or capacitive charging through structural water wires is not apparent.

The results above demonstrate that changes in surface hydration are responsible for the conductance dependence on water vapor pressure. To correlate these observations with the physical structure, diffraction studies were used to identify the orientation of the Miller indices with respect to the electrical contact points on the crystal. The contact points are on the (001) crystal face near

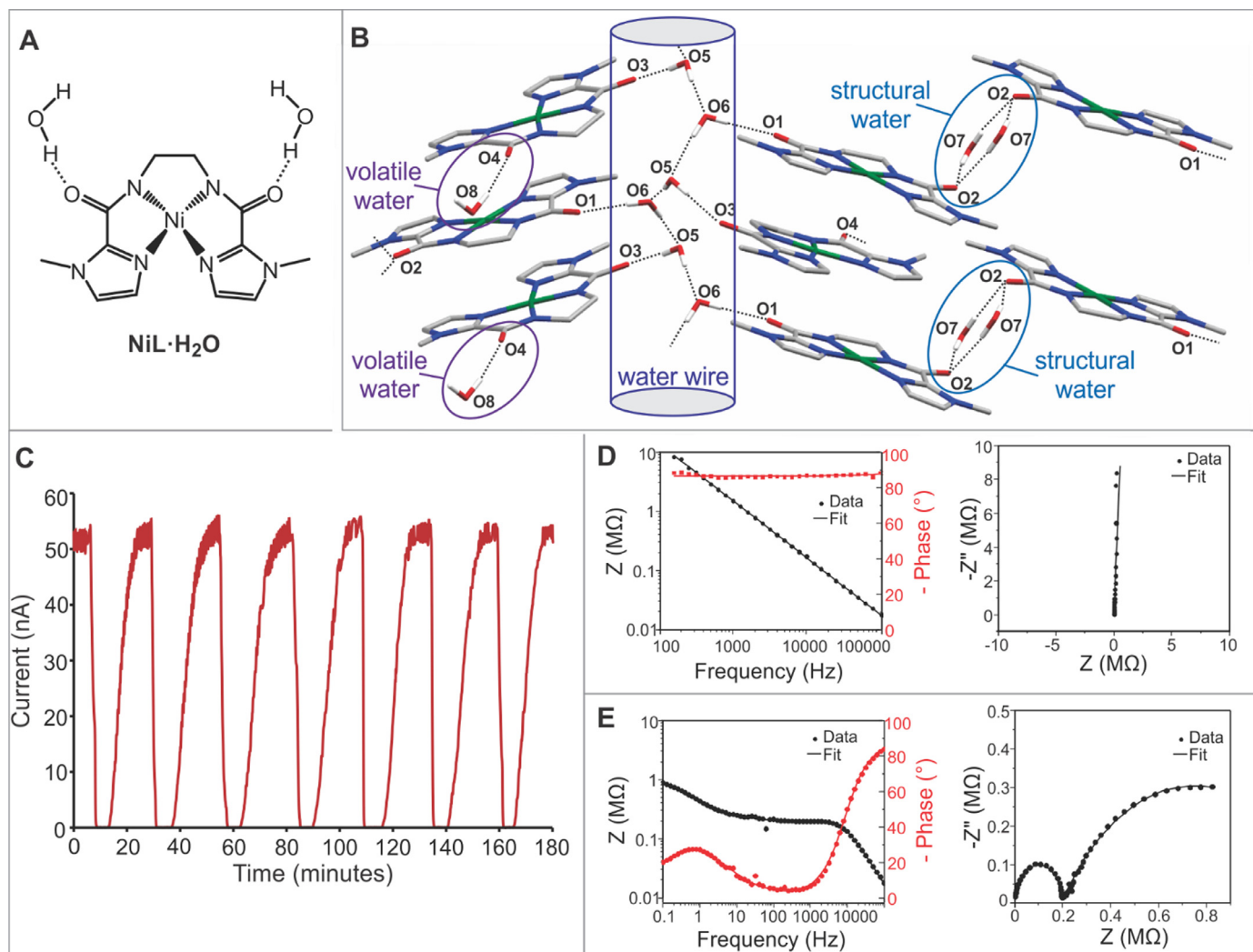


Fig. 1. A) Stick drawing of the chemical structure of $\text{NiL} \cdot \text{H}_2\text{O}$. B) Illustration of the extended hydrogen bonding network in $\text{NiL} \cdot \text{H}_2\text{O}$ highlighting the positions of the water wire (O5 and O6), structural water (O7), and volatile water (O8) relative to the nickel complex. C) Current across the 001 crystal face of $\text{NiL} \cdot \text{H}_2\text{O}$ under alternating wet and dry conditions. Maximum currents are observed under wet conditions and minimum currents occur under dry conditions. D) Bode (left) and Nyquist (right) representations of impedance data for $\text{NiL} \cdot \text{H}_2\text{O}$ under dry conditions. Dots represent individual data points, while lines represent the equivalent circuit fit. E) Bode (left) and Nyquist (right) representations of impedance data for $\text{NiL} \cdot \text{H}_2\text{O}$ under wet conditions. Dots represent individual data points, while lines represent the equivalent circuit fit.

the (100) edge (Fig. 2A). This positions the 1D water wires perpendicular to the electrical contacts with a distance of 23.767(2) Å between individual water wires (Fig. 2B). Individual water wires composed of O5 and O6 water molecules are arranged as $\text{C}^2_2(4)$ coiled chains using the graph set notation (Fig. S8) [41]. The 1D wires are anchored by carboxamide oxygens (O1 and O3) through additional H-bonds. Between the 1D water wires are two additional water molecules. The structural water molecule O7 is H-bonded in a $\text{R}^2_4(8)$ ring motif with O2 carboxamide oxygens. The volatile O8 water molecule (not shown) sits nearest the 1D water chain 7.68 and 7.65 Å from O5 and O6, respectively, and is in close contact with O7, 4.02 Å. Notably, O8 only participates in one H-bond consistent with its lower occupancy (20%) in the crystal lattice.

The presence of four distinct locations for the waters of hydration within the crystal and additional surface associated waters, raises the question as to which water is removed under the dry conditions. To probe this, a single crystal of $\text{NiL} \cdot \text{H}_2\text{O}$ was held under vacuum to reduce the $P_{\text{H}_2\text{O}}$ to 8 torr for 15 min. Thermogravimetric analysis (TGA) on as-isolated, conductive crystals (Fig. S9) and non-conductive crystals obtained after 15 min of vacuum exposure (Fig. 2C) show equivalent mass near 100°C consistent with 1.6 water molecules in the crystal lattice. X-ray powder diffrac-

tion (Fig. S10A) and single crystal unit cell determinations confirm the crystal structure of $\text{NiL} \cdot \text{H}_2\text{O}$ remains intact after 15 min vacuum exposure. Prolonged vacuum exposure overnight to remove more strongly H-bonded water molecules effectively dehydrates the crystal lattice as shown by TGA (Fig. 2D), x-ray powder diffraction (Fig. S10B), and the presence of powder rings in the single crystal x-ray diffraction pattern. Notably, conductivity loss after complete dehydration of the crystal lattice is irreversible consistent with the loss of the framework organization.

The reversible conductivity observed when the crystal is exposed to vacuum for shorter times (Fig. 1C) is consistent with the loss of surface hydration and retention of waters of hydration in the crystal lattice. The absence of the non-capacitive charge transfer pathway under these dry conditions, as determined by EIS studies, results from the loss of loosely held surface water, which is responsible for the reversible changes in conductivity between wet and dry conditions. That is, changes in surface hydration are responsible for the effects as the lattice hydration remains constant during the experiment. These results show the waters of hydration within the crystal of $\text{NiL} \cdot \text{H}_2\text{O}$ are necessary, but not sufficient, for a conductive water network on the crystal surface. The water of hydration initiates assembly of additional surface bound water, which confers increased conductivity.

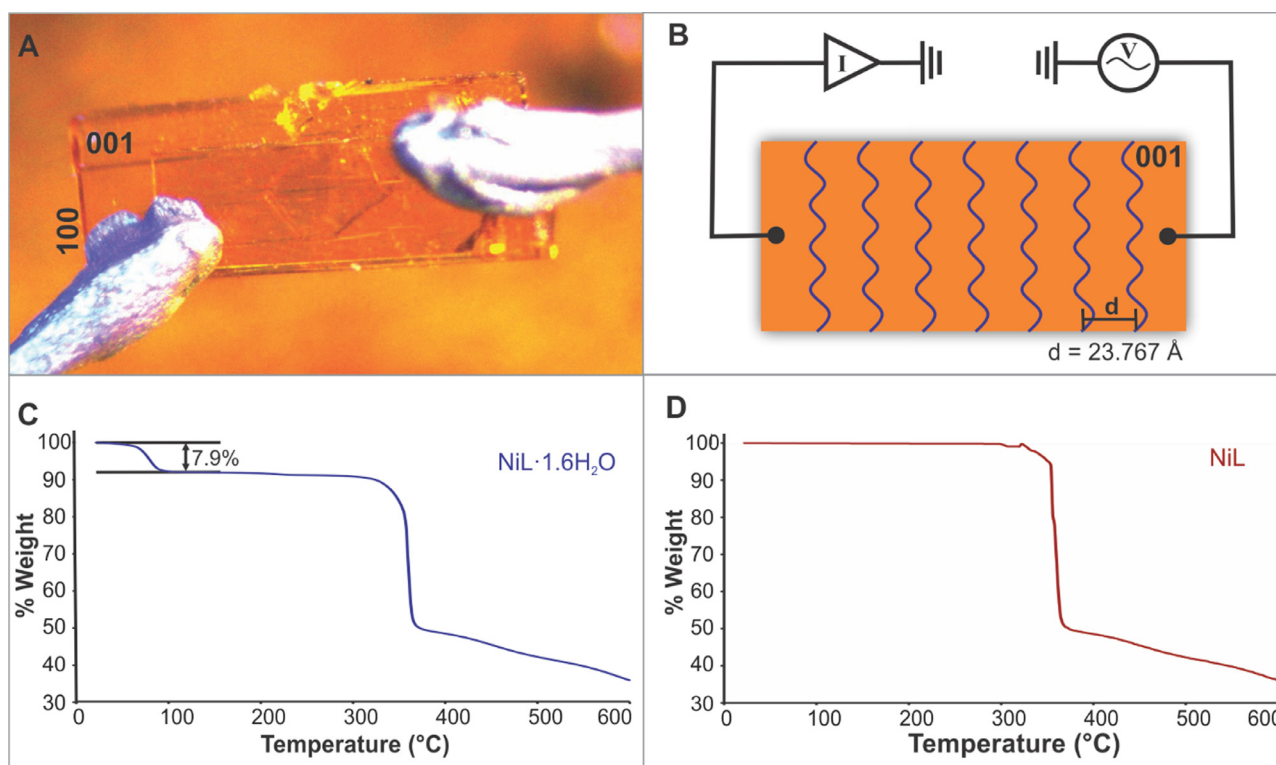


Fig. 2. A) Photograph of the 001 face of a NiL·H₂O crystal with silver epoxy resin leads attached near the 100 edges. B) Representation of the two-probe AC resistance measurements setup showing the orientation of the water wires (blue lines) on the 001 surface relative to the contact points. C) Thermogravimetric analysis data for NiL·H₂O after short (15 min) vacuum exposure consistent with the initial formula containing 1.6 waters of hydration, NiL·H₂O. D) Thermogravimetric analysis data for NiL·H₂O after long (overnight) vacuum exposure consistent with the lattice dehydrated state, NiL.

Next, we evaluated the change in conductivity of NiL·H₂O as a function of water vapor pressure. The crystal used in this study displayed a saturating current of 56 ± 1 nA at $P_{\text{H}_2\text{O}}$ of 17 torr. Lowering the vapor pressure results in a decrease in the steady state current (Fig. 3A and Table S5) until dry conditions are achieved at $P_{\text{H}_2\text{O}} = 12$ torr and below. Overall, the current response shows a sigmoidal dependence on $P_{\text{H}_2\text{O}}$ (Fig. 3B) with saturation at $P_{\text{H}_2\text{O}} > 17$ torr. The inflection point of the curve occurs at $P_{\text{H}_2\text{O}}$ 15.5 torr yielding an equilibrium constant for water adsorption (K) of 0.0645 torr^{-1} .

The rate of conversion between the dry and wet conditions was evaluated as a function of $P_{\text{H}_2\text{O}}$. Starting from dry conditions, the time required to obtain saturating current depends on $P_{\text{H}_2\text{O}}$ (Fig. 3C). The current shows an initial lag, followed by a more rapid increase and can be fit with two sequential steps (Fig. S11–S14 and Table S6). The observed rate constant at 26°C for the first step shows a half-order dependence on the $P_{\text{H}_2\text{O}}$ with a calculated $k_1 = (7.37 \pm 0.05) \times 10^{-3} \text{ torr}^{-0.5} \text{ s}^{-1}$ (Fig. 3D). The first step is associated with adsorption of water into surface exposed sites in the crystal (O5–O8) that dissociate under dry conditions. The observed rate constants at 26°C for the more rapid second step are third-order dependent on the $P_{\text{H}_2\text{O}}$ with a calculated $k_2 = (1.13 \pm 0.06) \times 10^{-6} \text{ torr}^{-3} \text{ s}^{-1}$ (Fig. 3E). The second step is associated with formation of the organized water network and includes additional water molecules adsorbed on the crystal surface.

Modulation of the crystal environment between dry and wet conditions tunes conductivity by changing the hydration of the crystal surface via a two-step process. Under dry conditions (Fig. 4A) the surface exposed 1D water chains are isolated due to vacancies of the water, O8, sites on the surface consistent with the x-ray structure and the TGA data above. Under these dry conditions, the crystal acts as a capacitor. Upon exposure to water vapor, the volatile sites are slowly populated (Fig. 4B) resulting in a slight

increase in conductivity. Once the volatile sites are occupied, we envision that additional water molecules begin to assemble on the surface connecting the 1D water wires through the structural and volatile water sites (Fig. 4C). This loosely held network provides a pathway for charge transfer between the electrodes. Finally, an organized, extended network is achieved resulting in current saturation associated with wet conditions (Fig. 4D).

3. Conclusions

The remarkable feature of this system is the ability to tune conductivity by modulation of the surface hydration of a crystal while maintaining a constant lattice hydration. Discrete water sites on the surface of the crystal act as nucleation centers for the formation of linkages that transform isolated 1D water wires into conducting 2D water networks. This is in contrast to related systems that rely on hydration/dehydration of the material lattice to induce structural changes within the bulk of the material. To our knowledge, this surface phenomenon is more typical to the behavior of thin films and this is the first discrete small molecule complex to display this behavior. This study demonstrates the utility of using the functional groups and packing of a small molecule to create imprinted elements on a surface for the bonding and organization of water or other small molecules. This approach allows systematic structure-function variation to modulate the identity and relative location of chemical functional groups to tailor the strength and selectivity of the interactions between the surface and the surface adsorbed water or other surface bound species.

4. Material and methods

Material and methods details are described in the Supplementary Information available online. There the reader will find syn-

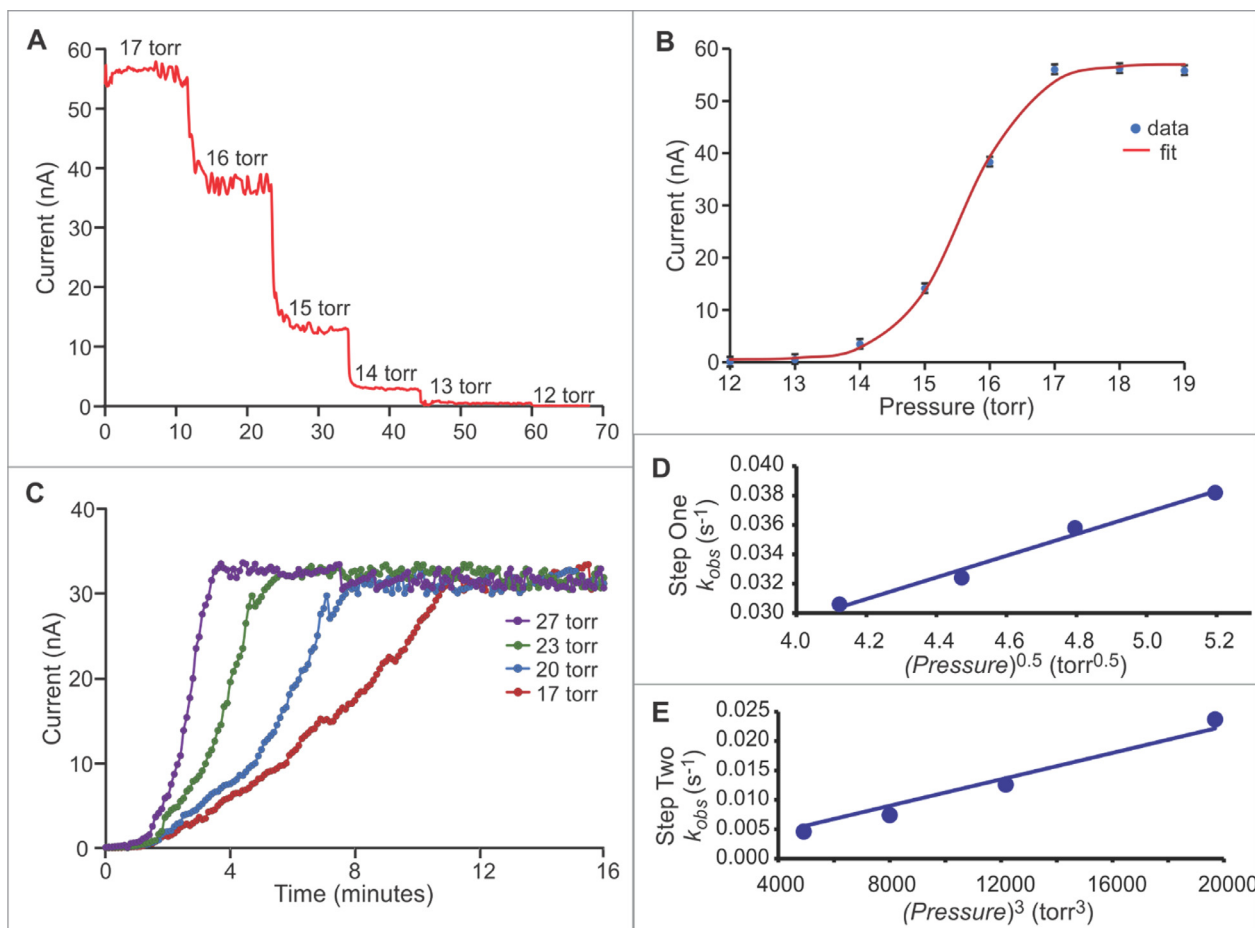


Fig. 3. Plots of current across the 001 face of a NiL-H₂O crystal under various conditions A) Modulation of current as a function of P_{H_2O} from wet (17 torr) to dry (12 torr) conditions. B) Equilibrium current, with error bars, as a function of P_{H_2O} from wet (17 torr) to dry (12 torr) conditions. Data was fit to a sigmoidal equation (see *Supplementary Materials* for details). C) Increase in current as a function of time upon transition from dry to wet conditions at various P_{H_2O} and a constant temperature of 26°C. D) Plot of the observed rate constant k_{obs} (s⁻¹) for step one versus $(P_{H_2O})^{0.5}$. Data are represented by circles that encompass the standard error in k_{obs} . The solid line is the best fit line $y = 0.0074x$; $R^2 = 0.9835$. E) Plot of the observed rate constant k_{obs} (s⁻¹) for step two versus $(P_{H_2O})^3$. Data are represented by circles that encompass the standard error in k_{obs} . The solid line is the best fit line $y = (1.1 \times 10^{-6})x$; $R^2 = 0.9670$.

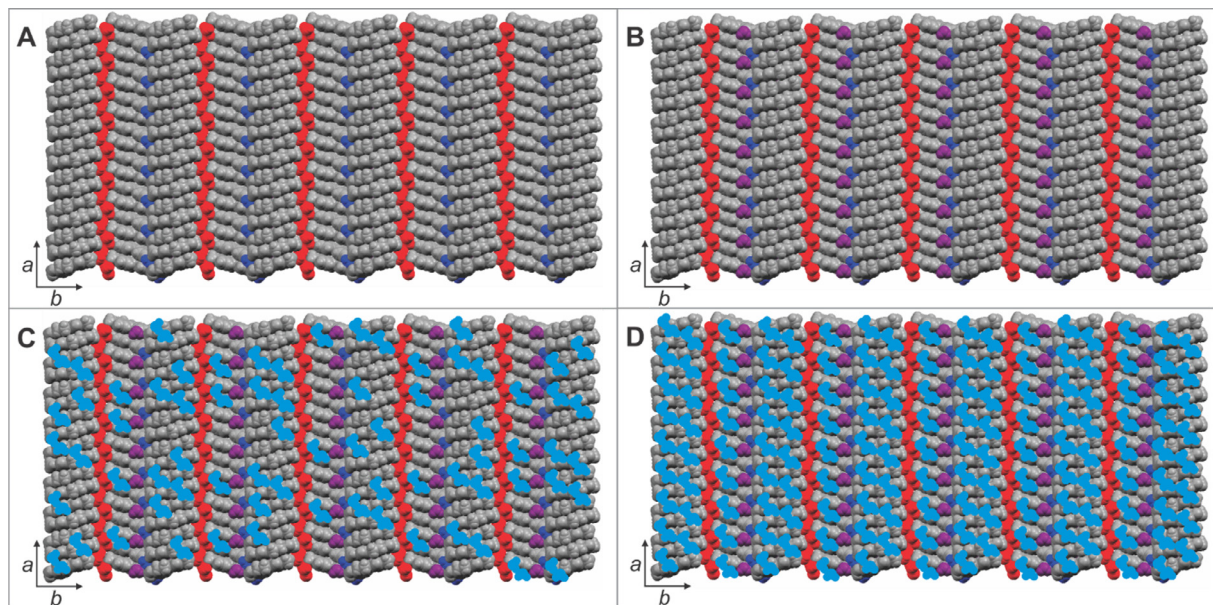


Fig. 4. Illustration of the changes in the 001 surface of NiL-H₂O (NiL = grey, O5-O6 water channel = red, O7 structural water = dark blue, O8 volatile water = purple, surface adhered water = light blue) under dry conditions (A) upon exposure to wet conditions over time (B – D). Contact points (not shown) are located near the 100 edge. Charge propagation occurs along the b -direction on the 001 surface. A) Under dry conditions, volatile water is absent and the crystal acts like a capacitor. B) Exposure to wet conditions populates volatile water positions leading to a small increase in conductivity. C) The accumulation of surface water upon longer exposure to wet conditions provides charge propagation pathways and larger increases in conductivity. D) Saturation with surface water results in an extended charge propagation network pathways with maximum conductivity.

thetic and crystallization methods, a more detailed description of the electrical resistance measurements, details of the electrochemical impedance spectroscopy measurements, procedures for thermal gravimetric analyses, and kinetic data.

Author Contributions

R.M.B., C.A.G., and G.S. conceived the project. N.S., B.C.F. and G.S. designed and carried the electrical resistance measurements. A.J.G. and G.G. designed and carried the electrochemical impedance spectroscopy experiments. M.S.M., O.H., D.T.H., and C.A.G. performed the collection and analysis of x-ray data. C.A.G., R.M.B., O.H. and N.S. were primarily responsible for drafting the manuscript. All authors contributed to editing of the manuscript for final approval prior to submission.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

This research was supported in part by the [National Science Foundation CHE-1665136 \(CAG\)](#) and [CHE-1800245 \(RMB\)](#). MSM thanks the [Department of Energy \(DEFG02-08CH11538\)](#) and the Kentucky Research Challenge Trust Fund for upgrade of our X-ray facilities. NS thanks Dr. Rong Zhao for training and assistance with initial experiments using the two-probe resistance measurement system.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.apmt.2020.100895](https://doi.org/10.1016/j.apmt.2020.100895).

References

- [1] J. Monroe, M. Barry, A. DeStefano, P.A. Gokturk, S. Jiao, D. Robinson-Brown, T. Webber, E.J. Crumlin, S. Han, M.S. Shell, Water structure and properties at hydrophilic and hydrophobic surfaces, *Annu. Rev. Chem. Biomol. Eng.* 11 (2020) 523–557, doi:[10.1146/annurev-chembioeng-120919-114657](https://doi.org/10.1146/annurev-chembioeng-120919-114657).
- [2] E. Brini, C.J. Fennell, M. Fernandez-Serra, B. Hribar-Lee, M. Lukšič, K.A. Dill, How water's properties are encoded in its molecular structure and energies, *Chem. Rev.* 117 (2017) 12385–12414, doi:[10.1021/acs.chemrev.7b00259](https://doi.org/10.1021/acs.chemrev.7b00259).
- [3] M.-C. Bellissent-Funel, A. Hassanali, M. Havenith, R. Henchman, P. Pohl, F. Sterpone, D. van der Spoel, Y. Xu, A.E. Garcia, Water determines the structure and dynamics of proteins, *Chem. Rev.* 116 (2016) 7673–7697, doi:[10.1021/acs.chemrev.5b00664](https://doi.org/10.1021/acs.chemrev.5b00664).
- [4] J. Esque, M.S.P. Sansom, M. Baaden, C. Oguey, Analyzing protein topology based on Laguerre tessellation of a pore-traversing water network, *Sci. Rep.* 8 (2018) 13540, doi:[10.1038/s41598-018-31422-5](https://doi.org/10.1038/s41598-018-31422-5).
- [5] B. Gong, Artificial water channels: inspiration, progress, and challenges, *Faraday Discuss.* 209 (2018) 415–427, doi:[10.1039/C8FD00132D](https://doi.org/10.1039/C8FD00132D).
- [6] A. Horner, C. Siligan, A. Cornean, P. Pohl, Positively charged residues at the channel mouth boost single-file water flow, *Faraday Discuss.* 209 (2018) 55–65, doi:[10.1039/C8FD00050F](https://doi.org/10.1039/C8FD00050F).
- [7] M. Barboiu, P.-A. Cazade, Y.L. Duc, Y.-M. Legrand, A. van der Lee, B. Coasne, Polarized water wires under confinement in chiral channels, *J. Phys. Chem. B* 119 (2015) 8707–8717, doi:[10.1021/acs.jpbc.5b03322](https://doi.org/10.1021/acs.jpbc.5b03322).
- [8] M. Barboiu, A. Gilles, From natural to bioassisted and biomimetic artificial water channel systems, *Acc. Chem. Res.* 46 (2013) 2814–2823, doi:[10.1021/ar400025e](https://doi.org/10.1021/ar400025e).
- [9] Y. Huo, H. Zeng, Sticky"-ends-guided creation of functional hollow nanopores for guest encapsulation and water transport, *Acc. Chem. Res.* 49 (2016) 922–930, doi:[10.1021/acs.accounts.6b00051](https://doi.org/10.1021/acs.accounts.6b00051).
- [10] S. Sharma, P. Biswas, Unusual dynamics of hydration water around motor proteins with long-ranged hydrodynamic fluctuations, *Physica A* 534 (2019) 122045, doi:[10.1016/j.physa.2019.122045](https://doi.org/10.1016/j.physa.2019.122045).
- [11] L.E. Cheruzel, M.S. Pometun, M.R. Cecil, M.S. Mashuta, R.J. Wittebort, R.M. Buchanan, Structures and solid-state dynamics of one-dimensional water chains stabilized by imidazole channels, *Angew. Chem. Int. Ed.* 42 (2003) 5452–5455, doi:[10.1002/anie.200352157](https://doi.org/10.1002/anie.200352157).
- [12] F. Jian, E. Liu, J. Xu, A water cluster conduit in crystal, *Molecules* 22 (2017) 2278, doi:[10.3390/molecules22122278](https://doi.org/10.3390/molecules22122278).
- [13] Y.-M. Legrand, M. Michau, A. van der Lee, M. Barboiu, Homomeric and heteromeric self-assembly of hybrid ureido-imidazole compounds, *Crystengcomm* 10 (2008) 490–492, doi:[10.1039/b717015g](https://doi.org/10.1039/b717015g).
- [14] B.C.R. Sansam, K.M. Anderson, J.W. Steed, A simple strategy for crystal engineering water clusters, *Cryst. Growth Des.* 7 (2007) 2649–2653, doi:[10.1021/cg700932s](https://doi.org/10.1021/cg700932s).
- [15] P.K. Thallapally, G.O. Lloyd, J.L. Atwood, L.J. Barbour, Diffusion of water in a nonporous hydrophobic crystal, *Angew. Chem. Int. Ed.* 44 (2005) 3848–3851, doi:[10.1002/anie.200500749](https://doi.org/10.1002/anie.200500749).
- [16] S. Supriya, S.K. Das, Small water clusters in crystalline hydrates, *J. Cluster Sci.* 14 (2003) 337–366, doi:[10.1023/B:JOCL.000005068.77622.a4](https://doi.org/10.1023/B:JOCL.000005068.77622.a4).
- [17] B.L. de Groot, H. Grubmüller, Water permeation across biological membranes: mechanism and dynamics of aquaporin-1 and GlpF, *Science* 294 (2001) 2353–2357, doi:[10.1126/science.1062459](https://doi.org/10.1126/science.1062459).
- [18] C. Dellago, M.M. Naor, G. Hummer, Proton transport through water-filled carbon nanotubes, *Phys. Rev. Lett.* 90 (2003) 105902, doi:[10.1103/PhysRevLett.90.105902](https://doi.org/10.1103/PhysRevLett.90.105902).
- [19] N. Agmon, The Grotthuss Mechanism, *Chem. Phys. Lett.* 244 (1995) 456–462, doi:[10.1016/0009-2614\(95\)00905-j](https://doi.org/10.1016/0009-2614(95)00905-j).
- [20] K.D. Kreuer, Proton conductivity: Materials and applications, *Chem. Mater.* 8 (1996) 610–641, doi:[10.1021/cm950192a](https://doi.org/10.1021/cm950192a).
- [21] G.J. Halder, C.J. Kepert, Single crystal to single crystal structural transformations in molecular framework materials, *Aust. J. Chem.* 59 (2006) 597–604, doi:[10.1071/ch06322](https://doi.org/10.1071/ch06322).
- [22] J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin, X.-M. Chen, Single-crystal X-ray diffraction studies on structural transformations of porous coordination polymers, *Chem. Soc. Rev.* 43 (2014) 5789–5814, doi:[10.1039/c4cs00129j](https://doi.org/10.1039/c4cs00129j).
- [23] S.-S. Bao, N.-Z. Li, J.M. Taylor, Y. Shen, H. Kitagawa, L.-M. Zheng, Co-Ca Phosphonate showing humidity-sensitive single crystal to single crystal structural transformation and tunable proton conduction properties, *Chem. Mater.* 27 (2015) 8116–8125, doi:[10.1021/acs.chemmater.5b03897](https://doi.org/10.1021/acs.chemmater.5b03897).
- [24] H. Bunzen, A. Javed, D. Klawinski, A. Lamp, M. Grzywa, A. Kalytta-Mewes, M. Tiemann, H.-A.K. von Nidda, T. Wagner, D. Volkmer, Anisotropic water-mediated proton conductivity in large Iron(II) Metal-organic framework single crystals for proton-exchange membrane fuel cells, *ACS Appl. Nano Mater.* 2 (2019) 291–298, doi:[10.1021/acsami.8b01902](https://doi.org/10.1021/acsami.8b01902).
- [25] A.D.G. Firmino, R.F. Mendes, M.M. Antunes, P.C. Barbosa, S.M.F. Vilela, A.A. Valente, F.M.L. Figueiredo, J.P.C. Tomé, F.A.A. Paz, Robust multifunctional Yttrium-based metal-organic frameworks with breathing effect, *Inorg. Chem.* 56 (2017) 1193–1208, doi:[10.1021/acs.inorgchem.6b02199](https://doi.org/10.1021/acs.inorgchem.6b02199).
- [26] S. Tominaka, F.-X. Coudert, T.D. Dao, T. Nagao, A.K. Cheetham, Insulator-to-proton-conductor transition in a dense metal-organic framework, *J. Am. Chem. Soc.* 137 (2015) 6428–6431, doi:[10.1021/jacs.5b02777](https://doi.org/10.1021/jacs.5b02777).
- [27] R. Li, S.-H. Wang, X.-X. Chen, J. Lu, Z.-H. Fu, Y. Li, G. Xu, F.-K. Zheng, G.-C. Guo, Highly Anisotropic and Water Molecule-Dependent Proton Conductivity in a 2D Homochiral Copper(II) Metal-Organic Framework, *Chem. Mater.* 29 (2017) 2321–2331, doi:[10.1021/acs.chemmater.6b05497](https://doi.org/10.1021/acs.chemmater.6b05497).
- [28] L. Qin, Y.-Z. Yu, P.-Q. Liao, W. Xue, Z. Zheng, X.-M. Chen, Y.-Z. Zheng, A "Molecular Water Pipe": a giant tubular cluster {Dy72} exhibits fast proton transport and slow magnetic relaxation, *Adv. Mater.* 28 (2016) 10772–10779, doi:[10.1002/adma.201603381](https://doi.org/10.1002/adma.201603381).
- [29] P.L. Knöchel, P.J. Keenan, C. Loh, C. Reitz, R. Witte, K.S. Knight, A.J. Wright, H. Hahn, P.R. Slater, O. Clemens, Synthesis, structural characterisation and proton conduction of two new hydrated phases of barium ferrite BaFeO_{2.5-x}(OH)_{2x}, *J. Mater. Chem. A* 4 (2016) 3415–3430, doi:[10.1039/C5TA06383C](https://doi.org/10.1039/C5TA06383C).
- [30] H.-B. Luo, M. Wang, J. Zhang, Z.-F. Tian, Y. Zou, X.-M. Ren, Open-framework chalcogenide showing both intrinsic anhydrous and water-assisted high proton conductivity, *ACS Appl. Mater. Interfaces* 10 (2018) 2619–2627, doi:[10.1021/acsami.7b17189](https://doi.org/10.1021/acsami.7b17189).
- [31] M. Yoon, K. Suh, H. Kim, Y. Kim, N. Selvapalam, K. Kim, High and highly anisotropic proton conductivity in organic molecular porous materials, *Angew. Chem. Int. Ed.* 50 (2011) 7870–7873, doi:[10.1002/anie.201101777](https://doi.org/10.1002/anie.201101777).
- [32] D. Umeyama, S. Horike, M. Inukai, T. Itakura, S. Kitagawa, Inherent proton conduction in a 2D coordination framework, *J. Am. Chem. Soc.* 134 (2012) 12780–12785, doi:[10.1021/ja304693r](https://doi.org/10.1021/ja304693r).
- [33] A. Javed, T. Wagner, S. Wöhlbrandt, N. Stock, M. Tiemann, Proton conduction in a single crystal of a phosphonate-sulfonate-based coordination polymer: mechanistic insight, *Chem. Phys. Chem.* 21 (2020) 605–609, doi:[10.1002/cphc.202000102](https://doi.org/10.1002/cphc.202000102).
- [34] R.J. Kirkpatrick, A.G. Kalinichev, J. Wang, Molecular dynamics modelling of hydrated mineral interlayers and surfaces: structure and dynamics, *Mineral. Mag.* 69 (2005) 289–308, doi:[10.1180/0026461056930251](https://doi.org/10.1180/0026461056930251).
- [35] A. Bankura, A. Chandra, Proton transfer through hydrogen bonds in two-dimensional water layers: A theoretical study based on ab initio and quantum-classical simulations, *J. Chem. Phys.* 142 (2015) 44701–44713, doi:[10.1063/1.4905495](https://doi.org/10.1063/1.4905495).

- [36] G. Zundel, H. Metzger, Energiebänder der tunnelnden Überschuß-Protonen in flüssigen Säuren. Eine IR-spektroskopische Untersuchung der Natur der Gruppierungen H_5O_2^+ , *Z. Phys. Chem.* 58 (1968) 225–245, doi:[10.1524/zpch.1968.58.5.6.225](https://doi.org/10.1524/zpch.1968.58.5.6.225).
- [37] M. Eigen, Proton transfer, acid-base catalysis, and enzymatic hydrolysis. part i: elementary processes, *Angew. Chem. Int. Ed.* 3 (1964) 1–19, doi:[10.1002/anie.196400011](https://doi.org/10.1002/anie.196400011).
- [38] M. Park, I. Shin, N.J. Singh, K.S. Kim, Eigen and Zundel forms of small protonated water clusters: Structures and infrared spectra, *J. Phys. Chem. A* 111 (2007) 10692–10702, doi:[10.1021/jp073912x](https://doi.org/10.1021/jp073912x).
- [39] S. Borini, R. White, D. Wei, M. Astley, S. Haque, E. Spigone, N. Harris, J. Kivioja, T. Ryhänen, Ultrafast graphene oxide humidity sensors, *ACS Nano* 7 (2013) 11166–11173, doi:[10.1021/nn404889b](https://doi.org/10.1021/nn404889b).
- [40] N. Saraei, O. Hietsoi, B.C. Frye, A.J. Gupta, M.S. Mashuta, G. Gupta, R.M. Buchanan, C.A. Grapperhaus, Water wire clusters in isostructural Cu(II) and Ni(II) complexes: synthesis, characterization, and thermal analyses, *Inorg. Chim. Acta* 492 (2019) 268–274, doi:[10.1016/j.ica.2019.04.012](https://doi.org/10.1016/j.ica.2019.04.012).
- [41] M.C. Etter, J.C. MacDonald, J. Bernstein, Graph-set analysis of hydrogen-bond patterns in organic crystals, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* 46 (1990) 256–262, doi:[10.1107/s0108768189012929](https://doi.org/10.1107/s0108768189012929).