Enhanced anhydrous proton conduction in binary mixtures of 1H-imidazole–1H-1,2,3-triazole based compounds†

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What is the impact of mixing two proton-conducting heterocycles on proton conductivity? Herein we answer this question through our investigations on two linear rod-like compounds 2-(4-(dodecyloxy)phenyl)-1H-imidazole (4) and 5-(4-(dodecyloxy)phenyl)-1H-1,2,3-triazole (10). We have found that mixtures of molecules 4 and 10 at certain compositions show enhanced proton conductivity compared to their pure components. We attribute the increased conductivity in these materials to the increased charge density due to facile co-ionization and increased mobility due to the incorporation of long alkyl chains, which prevent crystallization of protogenic groups while maintaining the required hydrogen bonded network. Our results suggest a new strategy for enhancing intrinsic proton conductivity in heterocyclic systems.

1 Introduction

Proton transporting materials that have high intrinsic proton conductivity are highly desirable for fuel cell applications.1,2 For this purpose high boiling organic heterocycles such as 1H-imidazole or 1H-1,2,3-triazole have been considered due to their ability to form hydrogen bond networks similar to water.3–6 Proton conduction in these heterocycles is believed to occur through the Grotthuss mechanism wherein the protons are transported through non-diffusive pathways.6,7 In general, the magnitude of ion conductivity is described as:

\[
\sigma(T) = \sum n_i \mu_i q_i
\]

where \(\sigma(T)\) is the conductivity, \(T\) is the temperature and \(q_i\), \(n_i(T)\) and \(\mu_i\) are charge, concentration of the intrinsic charge carriers, and mobility of the charge, respectively.8 Eqn (1) further indicates that both the charge carrier mobility and the concentration of intrinsic charge carriers will have a profound impact on the overall proton conductivity. Furthermore, for efficient proton transport, it is imperative that the proton-transferring groups organize in such a way that a continuous pathway of protonic charge carriers exists, with enough flexibility for molecular reorientation of the hydrogen-bonded network.9–12 This can be achieved via immobilization of the heterocycles with flexible linkers (such as long alkyl chains), which satisfies both the requirements.13,14 At high temperature (above \(T_g\) for polymers and above \(T_m\) for small molecules), where the mobility of the heterocycles is high it is the number of intrinsic charge carriers that guides the resulting conductivity.15,16 For N-based heterocycles, however, this intrinsic charge carrier concentration is typically low (~0.1%), resulting from self-dissociation of the protogenic groups.5,17 Extrinsic doping with strong acids has been carried out to increase this concentration,6,18,19 but this approach often suffers from potential leaching at high temperatures and a reduction in the proton mobility due to the perturbed hydrogen bonded network upon acid-doping.7,17 Our initial findings on certain binary mixtures of 1H-imidazole and 1H-1,2,3-triazole show a significant enhancement in proton conductivity compared to either of the pure compounds.20 This result suggests that mixing slightly basic 1H-imidazole (pK \(_{a1}\) = 7.18, pK \(_{a2}\) = 14.52)21 with slightly acidic 1H-1,2,3-triazole (pK \(_{a1}\) = 1.17, pK \(_{a2}\) = 9.26)5,22 facilitates co-ionization, generating additional charge carriers consisting of imidazolium triazolate. It appears, therefore, that a viable strategy to increase charge carrier density and mobility is to incorporate complementary weak-acid and weak-base into a supramolecular structure.

As model systems we investigate linear rod-like compounds with a long alkyl chain at one end and heterocyclic functionality such as 1H-imidazole (4) or 1H-1,2,3-triazole (10) at the other end (Fig. 1). These systems have been designed such that interactions between the long alkyl chains and the protogenic groups will yield a nanoscale organization allowing continuous hydrogen bond pathways, which, coupled with dynamic
behaviour, may furnish high proton conductivities. Experiments with several composites of 4 and 10 (complementary mixtures of triazole and imidazole) were performed to understand the impact of effective charge carrier density on the overall proton conductivity. Additionally, by changing the protogenic group from 1H-1,2,3-triazole to 1H-imidazole in these small molecule systems, we are able to investigate the impact of each heterocycle in a nearly identical structural environment. This systematic study investigating the role of charge carrier density in a system with nanoscale domains is an important step towards setting the design criteria for co-polymers with complimentary heterocycles for next generation polymer electrolyte membranes.

2 Experimental section

2.1 Materials and characterization

All 1H and 13C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. Chemical shift (δ) and coupling constant (J) are reported in parts per million and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets, and m, multiplet. TGA was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ from room temperature to 600 °C under nitrogen. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo model DSC 822 differential scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J mol⁻¹) and Zn (692.7 K, 12 J mol⁻¹) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler-Toledo STAR® software system. Optical microscopy was performed on a Zeiss Axioscope Vario reflected light microscope under crossed polarizers, equipped with an Instec HCS62N hot stage. X-Ray scattering was done using an in-house setup from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000). It uses a 30 W microsource (Bede) with a 30 × 30 μm² spot size matched to a MaxFlux® optical system (Osmic) leading to a low-divergence beam of monochromatic CuKα radiation (wavelength λ = 0.1542 nm). After passing beam defining and guard pinholes, the beam of about 0.4 mm diameter enters the sample chamber. Samples were placed within a hot stage connected to an Omega CN76000 temperature controller. WAXS was performed using an image plate (maximum resolution 50 μm) positioned in the sample chamber at a distance of 139 mm. The whole system is evacuated. The actual scattering angles are calibrated using the accurately known reflections from silver behenate and tricosane. Mass spectroscopic methods were performed by the Mass Spectrometry Center at the University of Illinois, Urbana-Champaign. Impedance data were obtained using a Solartron 1260 frequency response analyzer in the range of 0.1 Hz to 10 MHz with a sinusoidal excitation voltage of 0.1 V root-mean-square amplitude. Vacuum dried samples were placed into a cavity (L = 0.029 cm long by A = 0.079 cm² cross-sectional area) of a PTFE tape spacer between two gold-coated stainless steel electrodes. The sample’s resistance to proton transport, R, was estimated by fitting a constant value to the plateau of impedance magnitude, which occurred within this frequency range. Conductivity was computed as σ = L/(RA). Measurements were conducted in an ESPEC SH-241 temperature control chamber between 40 °C and 150 °C with a sweep rate of 0.25 °C min⁻¹.

All reactions were carried out in oven-dried glassware (160 °C). The chemicals were purchased from major chemical suppliers (Acros, Sigma-Aldrich, Alfa-Aesar and TCI America) and were used without further purification unless otherwise noted. Triethylamine and dichloromethane were redistilled over anhydrous calcium hydride and stored over 4 Å molecular sieves under argon. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 230–400 mesh). Analytical thin layer chromatography was performed on a pre-coated silica gel glass plate with visualization under UV light. N-Bromosuccinimide (NBS) was recrystallized from water.

4-(Dodecyloxy)benzaldehyde (2), 1-(dodecyloxy)-4-ethylbenzene (8), and azidomethyl pivalate were synthesized according to the reported literature procedures, respectively.

2-(4-(Dodecyloxy)phenyl)-1,4,5-dihydro-1H-imidazole (3). Compound 3 was synthesized from compound 2 according to the procedure reported in the literature.26 Pale yellow solid. Yield: 69%. 1H NMR (CDCl₃, 400 MHz) δ 7.74 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 9.2 Hz, 2H), 4.86 (bs, 1H), 3.96 (t, J = 6.8 Hz, 2H), 3.76 (s, 4H), 1.78 (quintet, J = 6.8 Hz, 2H), 1.46–1.26 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H); 13C NMR (CDCl₃, 101 MHz) δ 164.4, 161.1, 128.5, 122.7, 114.2, 68.1, 31.9, 29.7, 29.66, 29.63, 29.60, 29.57, 29.39, 29.35, 29.18, 22.7, 14.1; HRMS (ESI) m/z calcd for C₂₁H₃₅N₂O⁺ [M + H⁺]: 331.2749; found: 331.2746.

2-(4-(Dodecyloxy)phenyl)-1H-imidazole (4). Compound 3 was converted to compound 4 according to the procedure reported in the literature.26 Pale yellow solid. Yield: 78%. 1H NMR (CDCl₃, 400 MHz) δ 7.75 (d, J = 8.8 Hz, 2H), 7.11 (s, 2H), 6.96 (d, J = 9.2 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 1.79 (quintet, J = 6.8 Hz, 2H), 1.47–1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); 13C NMR (CDCl₃, 101 MHz) δ 159.7, 146.9, 126.6, 122.9, 114.9, 68.1, 31.9, 29.67, 29.65, 29.61, 29.59, 26.41, 29.36, 29.2, 26.0, 22.7, 14.1; HRMS (ESI) m/z calcd for C₂₁H₃₅N₂O⁺ [M + H⁺]: 329.2593; found: 329.2587.

(5-(4-(Dodecyl)phenyl)-1,2,3-triazol-1-yl)methyl pivalate (9). In a single-necked round bottom flask a mixture of 8 (0.86 g, 3.0 mmol) and Cul (0.29 g, 1.5 mmol) were taken together under argon. To the mixture a solution of N,N-diisopropylethylamine (1.60 mL, 9.0 mmol), 0.72 g (4.50 mmol) of azidomethyl pivalate was added. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete (TLC), the product was dissolved in dichloromethane and washed with water. The organic layer was dried over magnesium perchlorate and concentrated to give a yellow solid. All products were purified by column chromatography using silica gel (60 Å, 230–400 mesh). Pale yellow solid. Yield: 78%. 1H NMR (CDCl₃, 400 MHz) δ 7.75 (d, J = 8.8 Hz, 2H), 7.11 (s, 2H), 6.96 (d, J = 9.2 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 1.79 (quintet, J = 6.8 Hz, 2H), 1.47–1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); 13C NMR (CDCl₃, 101 MHz) δ 159.7, 146.9, 126.6, 122.9, 114.9, 68.1, 31.9, 29.67, 29.65, 29.61, 29.59, 26.41, 29.36, 29.2, 26.0, 22.7, 14.1; HRMS (ESI) m/z calcd for C₂₁H₃₅N₂O⁺ [M + H⁺]: 329.2593; found: 329.2587.
in 40 mL of deoxygenated THF were added and stirred at 50 ºC for 12 h. The reaction mixture was cooled down to room temperature after 12 h and 60 mL of water was added. The organic layer was extracted with dichloromethane (2 × 60 mL), washed with water (2 × 50 mL), brine (2 × 50 mL), dried over anhydrous Na2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography (4 : 0.5 hexane–ethyl acetate) to afford 1.2 g of 9 (90%) as a white solid.

31H NMR (CDCl3, 400 MHz) 1H NMR (CDCl3, 400 MHz) δ 7.93 (s, 1H), 7.76 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.26 (s, 2H), 3.98 (t, J = 6.6 Hz, 2H), 1.79 (quintet, J = 6.8 Hz, 2H), 1.47–1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); 13C NMR (CDCl3, 101 MHz) δ 178.0, 159.4, 148.3, 127.1, 122.5, 120.0, 114.9, 69.7, 68.1, 31.9, 29.67, 29.64, 29.60, 29.59, 29.41, 29.36, 29.25, 26.8, 26.0, 22.7, 14.1; HRMS (ESI) m/z calcd for C26H42N3O3 [M + H]+: 444.3226; found: 444.3233.

5-(4-(Dodecyloxy)phenyl)-1H-1,2,3-triazole (10). In a single-necked round bottom flask 9 (1.1 g, 2.48 mmol) was dissolved in 30 mL of 0.5 M NaOH/THF (1 : 1 v/v mixture) and the mixture was heated at 50 ºC for 12 h. The reaction mixture was cooled down to room temperature, 20 mL water was added to it and pH was adjusted to 7.0 by dropwise addition of 1 M HCl. The mixture was filtered off, washed with water and dried under vacuum. The product was further purified by eluting through a small pad silica column (3% MeOH/CHCl3) to afford 10 as a white solid (quantitative yield). 1H NMR (DMSO-d6, 400 MHz) δ 14.95 (bs, 1H), 8.23 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.794 (quintet, J = 6.4 Hz, 2H), 1.44–1.27 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); 13C NMR (DMSO-d6, 101 MHz) δ 159.1, 127.4, 115.3, 67.9, 31.8, 29.5, 29.49, 29.46, 29.2, 29.19, 29.12, 25.9, 22.6, 14.1; HRMS (ESI) m/z calcd for C20H12N3O [M + H]+: 330.2545; found: 330.2549.

3 Results and discussions

3.1 Synthesis

2-(4-(Dodecylxyloxy)phenyl)-1H-imidazole (4) was synthesized from 4-hydroxybenzaldehyde (1) using the well-established literature procedure (Scheme 1).48 I was alkylated to 2 via Williamson’s ether synthesis; the latter was then converted to imidazole compound (3) by reacting with ethylenediamine.49 Swern oxidation48 of 3 furnished the desired imidazole derivative 4 as a pale yellow solid in 78% yield.

5-(4-(Dodecyloxy)phenyl)-1H-1,2,3-triazole (10) was obtained from 4-iodophenol in five steps (Scheme 2). 1-(Dodecylxyloxy)-4-ethynylbenzene (8) was obtained using Sonogashira coupling50 between compound 6 and TMS-acetylene using Cu(i)/Pd(0) in the presence of triethylamine as base, followed by TMS-cleavage under mild basic conditions. The alkyn group was then converted to pivolyloxymethyl protected 1,2,3-triazole moiety (9) using azide-alkyne-Huisgen dipolar cycloaddition reaction.30,31 The deprotection of the pivolyloxymethyl group in the presence of 0.5 M NaOH furnished compound 10 as a white solid.25

3.2 Thermal analysis

Thermal stability of 4, 10 and their mixtures was tested by thermogravimetric analysis (TGA) with a heating rate of 10 ºC min⁻¹ under a nitrogen atmosphere. Solid samples were kept in vacuo for 12 h before recording TGA data. DOPhIm (4) and DOPhTz (10) were mixed at different compositions and heated to 140 ºC for 1 h and then cooled (5 ºC min⁻¹) back slowly to room temperature to ensure intimate mixing. TGA plots of DOPhIm (4), DOPhTz (10) and their mixture of different compositions showed minimal weight loss before 230 ºC, indicating the thermal stability of the components at least up to 230 ºC (Fig. 2). A continuous weight loss was observed after 250 ºC, presumably due to decomposition of the hydrocarbon.

Thermal properties of DOPhTz (10) and DOPhIm (4) and their different compositions were studied by differential scanning calorimetry (DSC). DSC traces were recorded between −30 ºC and 200 ºC with a heating and cooling rate of 10 ºC min⁻¹ and 5 ºC min⁻¹, respectively. The composites were heated up to 200 ºC to remove any thermal history (first heating), followed by slow cooling (first cooling cycle) and subsequent heating (second heating cycle) (Fig. 3). Upon second heating DOPhTz (10) shows a single endotherm at 138.7 ºC, corresponding to the crystallization (K) to isotropic (I) transition. The transition is fully reversible as one exotherm corresponding to the crystallization arises at 130.7 ºC.

Fig. 2 Thermogravimetric analysis (TGA) of DOPhIm (4)–DOPhTz (10) composites (heating rate 10 ºC min⁻¹), the composites show minimal weight loss at least up to 230 ºC.
During the cooling cycle. Polarized optical micrographs (POM) of DOPhTz (10) above 140°C show no birefringence indicating an isotropic phase, while cooling the sample below 130°C results in birefringence, indicating crystallization (see Fig. S2 in the ESI†). Upon heating, DOPhIm (4) shows a broad endotherm at 131.3°C, corresponding to the crystal (K) to isotropic (I) phase transition, which was further supported by POM (Fig. S1 in the ESI†). Similar to DOPhTz (10), an exotherm arises at 119.3°C, indicating a fully reversible phase transition.

Most of the DOPhTz (10)–DOPhIm (4) composites exhibit two endotherms during heating, corresponding to two-phase transitions (K1 to K2 and K2 to I), which are fully reversible during the subsequent cooling cycles. However, the composites DOPhTz (10)–DOPhIm (4) = 40/60, 50/50 and 33.3/66.7 exhibit one endotherm during the heating cycle, corresponding to only one K to I transition. Details of transition temperatures and associated enthalpy changes are summarized in Table T1 of the ESI.†

The phase diagram of DOPhIm (4)–DOPhTz (10) composites is shown in Fig. 4. All the compositions are solid at room temperature and the melting points ($T_m$) of the composites are lower than the $T_m$ of either DOPhTz (10) or DOPhIm (4). As the mole fraction of DOPhIm (4) increases, the $T_m$ of the composites decreases until they form an equimolar mixture (50/50 DOPhIm (4)–DOPhTz (10)). Furthermore, two other composites DOPhIm (4)–DOPhTz (10) = 60/40 and 66.7/33.3 show similar $T_m$, indicating a range of eutectic compositions. When the mole fraction of DOPhIm (4) increases further, the $T_m$ of the composites again increases. The second melting peaks remain invariant with composition, located close to the $T_m$ of the eutectic compositions.

### 3.3 Anhydrous proton conduction

The temperature dependence of proton conductivities for various DOPhIm (4)–DOPhTz (10) composites were studied by impedance spectroscopy and are shown in Fig. 5. All samples were heated to 140°C, the highest temperature recorded, and conductivities were measured during slow cooling of the samples at the rate of 0.25°C min⁻¹. The anhydrous proton conductivity of DOPhIm (4) was $1.3 \times 10^{-4}$ S cm⁻¹ at 140°C, at least three orders of magnitude higher than that of DOPhTz (10) ($7.4 \times 10^{-7}$ S cm⁻¹) at the same temperature. A sharp slope change in log($\sigma$) vs. $1/T$ plot was observed for both DOPhIm (4) (at 123°C) and DOPhTz (10) (at 134°C), corresponding to the isotropic to crystalline phase transitions, correlating well with the transitions observed in DSC. This drastic drop in the conductivity curve further indicates that dynamic hydrogen bonding of a locally liquid-like state is critical for anhydrous proton conduction, in agreement with our previous report on discotic liquid crystalline proton conductors.

Fig. 6 shows the composition dependence of isothermal proton conductivities of different DOPhIm (4)–DOPhTz (10) composites. Neat DOPhTz (10) shows the lowest conductivity (e.g. $7.4 \times 10^{-7}$ S cm⁻¹ at 140°C) of any composition investigated, and increasing the mole fraction of DOPhIm (4) increases the proton conductivity until it reaches a local maximum at...
DOPhTz(10)–DOPhIm(4) = 50/50. At this 50/50 composition, a conductivity at 140 °C of $1.9 \times 10^{-4}$ S cm$^{-1}$ is observed, prior to a drop at DOPhTz(10)–DOPhIm(4) = 40/60. A similar trend is followed in the DOPhIm(4) rich range, wherein an increase in conductivity is observed at DOPhTz(10)–DOPhIm(4) = 12.5/87.5 (2.0 S cm$^{-1}$) at 140 °C prior to a decrease at DOPhTz(10)–DOPhIm(4) = 25/75. Among all the compositions, the highest conductivity is observed at DOPhTz(10)–DOPhIm(4) = 33.3/66.7, which is in the range of eutectic compositions. At 140 °C, the peak conductivity is $2.7 \times 10^{-4}$ S cm$^{-1}$, which is three orders of magnitude higher than the conductivity of neat DOPhTz (10) and slightly higher than neat DOPhIm (4) ($1.3 \times 10^{-4}$ S cm$^{-1}$) at the same temperature.

3.4 Powder X-ray scattering

Structures of neat DOPhTz (10), DOPhIm (4) and their equimolar composite DOPhTz(10)–DOPhIm(4) (50/50) were characterized using small- and wide-angle X-ray scattering. A distinct scattering peak is observed for neat DOPhTz (4) characterized using small- and wide-angle X-ray scattering. A distinct scattering peak is observed for neat DOPhTz (4) at different temperatures: samples were initially heated to 160 °C and subsequently cooled down to 80 °C and 25 °C. $I(q)$ values have been shifted vertically for clarity; (c) an illustration of the proposed structure of DOPhTz (10), which self-assembles into a head-to-head bilayer type packing.

Fig. 6 Isothermal anhydrous proton conductivities of different DOPhIm(4)–DOPhTz(10) composites as a function of DOPhIm (4) mole fraction.

Fig. 7 (a) DFT optimized at the B3LYP/6-31 G level of DOPhTz (10) estimating the molecular length of ~2.3 nm; (b) SAXS profile of DOPhTz (10) at different temperatures: samples were initially heated to 160 °C and subsequently cooled down to 80 °C and 25 °C. $I(q)$ values have been shifted vertically for clarity; (c) an illustration of the proposed structure of DOPhTz (10), which self-assembles into a head-to-head bilayer type packing.

Fig. 8 (a) DFT optimized at the B3LYP/6-31 G level of DOPhIm (4) estimating the molecular length of ~2.3 nm; (b) WAXS profile of DOPhIm (4) at different temperatures: samples were initially heated to 150 °C and subsequently cooled down to 80 °C and 50 °C. $I(q)$ values have been shifted vertically for clarity; (c) an illustration of the proposed structure of DOPhIm (4), which self-assembles into an interdigitated bilayer type packing.

dtemperature, causing them to become less extended, decreasing layer thickness and ordering in the system.

Fig. 8b shows wide-angle X-ray scattering (WAXS) of DOPhIm (4) recorded at variable temperatures. For comparison purposes, only the primary peak is shown in Fig. 8 (full WAXS spectrum is shown in the ESI Fig. S3†). Upon heating to 150 °C (beyond the phase transition temperature) no scattering peak was observed, indicating an isotropic phase, consistent with the DSC observation. Upon subsequent cooling to 80 °C, a well-resolved scattering peak appeared at $q = 1.91$ nm$^{-1}$, indicating the emergence of a characteristic length scale of 3.29 nm. This value is much lower than that for head-to-head packing of fully stretched dodecyl chains with imidazole functionality (~4.6 nm – Fig. 8a), and as such suggests an interdigitated structure obtained through side-to-side hydrogen bonding of adjacent imidazole groups (Fig. 8c). The single crystal X-ray structure of 2-[4-(decyloxy)-phenyl]-1H-imidazole reported in the literature exhibits extended chains of hydrogen bonding as well as
interdigitation of the imidazole rings, further supporting our speculation of an interdigitated bilayer type packing for DOPhIm (4) from variable temperature WAXS observations.

The structure of DOPhIm (4)–DOPhTz (10) composite (50/50) was further investigated using small angle X-ray scattering at various temperatures (Fig. 9). Upon heating to 130 °C, a diffuse broad peak arises at $q = 1.45$ nm$^{-1}$, indicating a poorly ordered, liquid-like material with a characteristic length scale of 4.34 nm. Upon cooling to 90 °C, a broad primary peak falls at $q = 1.34$ nm$^{-1}$ ($d = 4.69$ nm) and a second, diffuse peak centers on the original peak position at 130 °C ($q = 1.45$ nm$^{-1}$). Based on the persistence of the secondary peak, we speculate that a portion of the composite does not crystallize completely at this temperature (DSC cooling curve of 50/50 composite also shows a broad temperature regime of crystallization) and the peak location and breadth are due to the liquid-like nature of the aliphatic chains. Upon further cooling to 50 °C, a single peak persists at $q = 1.34$ nm$^{-1}$, suggesting complete crystallization. The characteristic length scale of 4.69 nm further indicates that the composite maintains a bilayer type ‘head-to-head’ stacking as observed in the packing of DOPhTz (10) component. It is also notable that the characteristic spacing ($d = 4.69$ nm) of the composite is higher than either DOPhIm (4) ($d = 3.29$ nm) or DOPhTz (10) ($d = 4.2$ nm), suggesting swelling of the head-to-head DOPhTz (10) domains via incorporation of interdigitating DOPhIm (4) (vide infra).

Combining these X-ray scattering results with our conductivity measurements provides insight into the nature of proton transport in both imidazole-DOPhIm (4) and triazole-containing (DOPhTz (10)) supramolecular architectures. It is known in the literature that in the crystal state, 1,2,3-triazole can exist in equal proportions of two tautomeric forms – $1H$-1,2,3-triazole and $2H$-1,2,3-triazole (in the gas phase $2H$-1,2,3-triazole is the predominant form while $1H$-1,2,3-triazole becomes increasingly more stable with an increase in the polarity of the medium). Based on these and further studies elucidating the possible proton transfer mechanisms in 1,2,3-triazole, we envision that DOPhTz (10) can exhibit two types of hydrogen bonding – extended bonds in the same layer using two side N atoms of the triazole ring (so-called imidazole-like pathway$^{33}$ – Fig. 10b), and localized bonds using the middle and one of the side N atoms (so-called pyrazole like pathway$^{33}$ – Fig. 10a). The head-to-head packing observed in DOPhTz (10) presumably supports the predominant existence of pyrazole-like pathways, resulting in hydrogen-bonded clusters with low charge mobility, yielding a low overall conductivity. Conversely, as X-ray scattering data support, DOPhIm (4) forms interdigitated structures through side-to-side hydrogen bonding between adjacent imidazole rings (Fig. 10c). Therefore, while DOPhTz (10) forms local hydrogen bonds, DOPhIm (4) forms extended one-dimensional hydrogen bonded networks, increasing protonic charge mobility and favouring long-range Grotthuss-type proton transport. Although the exact mechanism of proton transfer is still unclear and requires further attention, this result confirms that a change in the protogenic group from $1H$-imidazole to $1H$-1,2,3-triazole has a significant influence on charge mobility in supramolecular systems. While the nanoscale organization of protogenic groups has previously proven beneficial to proton conductivity, care must be taken to achieve a packing of heterocycles, which yields an extended hydrogen-bonded network versus locally hydrogen-bonded clusters.

Based solely on this argument of extended vs. local hydrogen bonding, DOPhIm (4), with the most imidazole-like hydrogen bonds, would have the highest conductivity of any composition measured. This is clearly not the case, however, as incorporating up to 50 percent DOPhTz (10) increases measured conductivity while presumably decreasing the occurrence of these favorable pathways. X-ray data for the equimolar mixture of DOPhTz (10)–DOPhIm (4) does suggest that DOPhIm (4) interpenetrates into the hydrogen bonded network of DOPhTz (10) and facilitates the formation of imidazole-like bonding in the composite (Fig. 10d), yet this alone cannot account for the enhanced conductivity of the composite mixtures. In order to understand the effect of complementary weak-acid–base
interactions between 1H-1,2,3-triazole and 1H-imidazole, we initiated a computational study.

### 3.5 Computational studies

To determine the trend in charge carrier density, a thermochemistry analysis was performed using the Gaussian09 software package. Structures of neutral, protonated, and deprotonated imidazole and 1,2,3-triazole were optimized using a 6-311G(d,p) basis set and the B3LYP hybrid density functional. Triazole may be protonated at adjacent or opposite positions, producing a total of six distinct auto- and cross-ionization reactions, listed below (Fig. 11). The standard Gibbs free energy for each isolated reactant under fictitious, ideal-gas conditions at STP was determined from a subsequent frequency calculation using Gaussian09. Standard reaction $\Delta G$ values for the six distinct reactions below were then computed and used to calculate each reaction $K_{eq}$, which is, in principle, proportional to the charge carrier density notwithstanding the environmental effects of solid-state packing. Because the solids synthesized and studied herein are likely to be low-dielectric materials, we do not expect solvation effects to control the actual ionization thermochemistry, and thus the gas-phase trends should remain qualitatively correct. These $K_{eq}$ values were referenced to the result for imidazole auto-ionization (Reaction 1 below) and are plotted on a logarithmic scale i.e., $K_{eq}$ values are shown as $\log_{10}(K_{eq}^{(n)}/K_{eq}^{(1)})$ where $K_{eq}^{(n)}$ is the $K_{eq}$ value for the $n^{th}$ reaction.

The standardized reaction $K_{eq}$ values are shown in Fig. 12. We note that the auto-ionization of imidazole is predicted to be more likely than that of triazole (Reactions 2a/2b). This is consistent with the experimental result that the conductivity of DOPhIm is greater than that of DOPhTz. In addition, we observe the particularly interesting result that $K_{eq}$ for Reaction 3, in which triazole protonates imidazole, is the largest value computed herein. This suggests that the charge carrier density is expected to be greatest in an imidazole–triazole mixture, which may lead to an increase in conductivity, all other things being equal. Although Reactions 4a and 4b also pertain to the mixture, they are rather unlikely because imidazole acts as the acid, which in contrast to the pKa values of imidazole and triazole as described above. These results suggest that the charge carrier density is expected to be greatest in mixtures of these functional groups, which is consistent with the experimentally obtained enhanced conductivity values.

### 4 Conclusion

We have synthesized two linear rod-like compounds based on 1H-imidazole and 1H-1,2,3-triazole proton transferring functionalities and investigated their anhydrous proton conductivities. The 1H-1,2,3-triazole-based compound DOPhTz (10) exhibited anhydrous proton conductivity at least three orders of magnitude lower than the conductivity of a 1H-imidazole-based compound DOPhIm(4) at the same temperature. The thermal behavior of these two compounds was found to be nearly identical, however, X-ray data support head-to-head bilayer type packing for DOPhTz (10) while an interdigitated structure through sideways hydrogen bonding is observed for DOPhIm (4). The enhanced conductivity of DOPhIm (4) is attributed to the formation of extended hydrogen bonded networks through an imidazole-like arrangement, while DOPhTz (10) primarily exists in pyrazole-like locally hydrogen bonded clusters. Mixing of the two materials in complementary acid–base composites demonstrates a potential increase in charge carrier density associated with co-ionization of 1H-imidazole and 1H-1,2,3-triazole, with maximum conductivity observed at a DOPhTz(10)–DOPhIm(4) ratio of 1/2. We conclude that to increase charge carrier density and mobility in anhydrous supramolecular systems, it is favourable to select complementary protogenic groups, which self-assemble into global hydrogen bonded networks. As a result, we are currently investigating new copolymers containing complementary acid–base pairs, which we hope to publish in due course.

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**Notes and references**

20. C. Versek and M. T. Tuominen, unpublished results.