Building Block Candidates for the Design of Proton Exchange Membranes: Maleimide and Its Homologues

Xuejiao Li¹, Liuming Yan^{2*}, Baohua Yue^{2*}

¹ Department of Physics, ² Department of Chemistry, Shanghai University, 99 Shangda Road,
Shanghai 200444, China

ABSTRACT

Density functional theory (DFT) calculations are applied to the study of proton transport in maleimide and its homologues, succinimide and phthalimide. The calculations reproduce correctly their structural characteristics and reveal the hydrogen bonding and proton hopping properties. Specifically, the calculations show that the potential barrier for proton transfer between two maleimide molecules is about $30.60 \text{ kcal}\cdot\text{mol}^{-1}$ mediated by one or two water molecules with correction of solvation effect by water, and will decrease to about $13.22 \text{ kcal}\cdot\text{mol}^{-1}$ if ethylphosphonic acid molecule is used as mediator with correction of solvation effect by phosphoric acid. In addition, the calculations also show that succinimide and phthalimide possess similar characteristics compared to maleimide. Finally, it is concluded that maleimide and its homologues are building block candidates for the design of high-temperature proton exchange membranes.

Keywords: proton exchange membrane; maleimide; succinimide; proton transport; density functional theory

* Corresponding author. Tel.: 8621-66132405, fax: 8621-66132405. E-mail: liuming.yan@t.shu.edu.cn (L.Y.)
yueyue902@163.com (B.Y.)

1. Introduction

High-temperature proton exchange membrane fuel cells (HT-PEMFCs) have been paid more and more attention as energy conversion devices because of higher energy conversion efficiency, noiseless operation and low pollution emission, especially the humidity-independent performances, enhanced electrocatalytic activity, and improved tolerance to impurities in fed-gas.¹ Nevertheless, the large scale commercialization of HT-PEMFCs depends heavily on the high-temperature performances of the proton exchange membranes (PEMs).² Though perfluorosulfonic acid polymers (PFSA) have achieved great progress in proton conductivity, chemical and electrochemical stability, the application of PFSA in PEMFCs is limited to temperatures that liquid water exists. At high temperature, the liquid water which hydrates the PFSA evaporates and the proton conductivity of PFSA degrades. Therefore, the development of novel proton conducting materials possessing high proton conductivity at high temperature and dehydrated or even anhydrous states is of the utmost importance.

Researches on PEMs are being conducted through experimental and theoretical efforts toward better performance at high temperature.³ For example, the proton conductivity and mechanical property can be improved by doping with inorganic compounds as water adsorption or retention materials,⁴⁻⁵ or by addition of organophosphates and azoles or amides to substitute water as hydration solvent.⁶⁻⁸ Studies have shown that membranes functionalized by phosphonic acid groups possess much better proton conductivity under dehydrated or even anhydrous states attributing to the self-dissociation and amphoteric character of the phosphonic acid group.⁹ The complex H-bonding network between phosphonic acid groups tethered to the polymer backbones result in the ability to conduct proton transport via the Grotthuss mechanism at high-temperature and low-humidity conditions.¹⁰⁻¹¹ During past years, great efforts have

been devoted to the synthesis of phosphonic acid functionalized polystyrene, poly(ether sulfone), polyimides and so on.¹²⁻¹⁵

Maleimide (MI) is also an interesting amphoteric molecule, with a dissociation constant $pK_a = 5.57$ evaluated from conductivity measurement (provided as **figure S1** in the supporting information). Actually, the H-bonding donor and acceptor of a MI molecule is similar to those of triazole molecules, both 1,2,3-triazole and 1,2,4-triazole, which are widely accepted as building blocks in the design of proton conducting materials at high temperature under a water deficient environment.¹⁶⁻¹⁷ As being shown in triazole, the tautomerization is an important characteristic for the proton transfer in hydrophilic compounds, which promotes long-range network structures for facile proton transfer.¹⁸ MI also shows abundant tautomerization pathways, especially with the mediation of other hydrophilic compounds, like organophosphates.¹⁵ In this aspect, Kalia *et al.* studied both the gas phase and water-assisted tautomerization of MI based on density functional theory,¹⁹ and Li *et al.* studied the proton transport in solid state MI using ab initio molecular dynamics simulations.²⁰ Based on these considerations, we propose that MI and its homologues, such as succinimide (SI) and phthalimide (PI), are building block candidates for the design of high-temperature proton conducting materials.

Density functional theory (DFT) calculations are widely applied to the study of proton transport in the field of proton exchange membrane. For example, Kreuer *et al.* applied DFT calculations to the study of sulfonic acid, phosphonic acid, and imidazole functionalized heptane in terms of bond rotational barrier of the functional groups and intermolecular H-bonding, and concluded that the imidazole is most labile when tethered to an alkyl chain and the energy penalty for proton transfer is greatest for imidazole and least for phosphonic acid.²¹ Yue *et al.*

studied the proton transfer pathways between ethylphosphonic acid (EPA) and 1,2,3-triazole using DFT calculations and concluded that the existence of EPA will greatly reduce the tautomerization activation energy of triazole.²² Zhou *et al.* developed a phosphotungstic acid functionalized and mesoporous silica-based high conductivity PEM, and revealed that the proton transfer involves both inter- and intra-molecular proton transfer pathways and evaluated the activation energy based on DFT calculations.²³ Inter- and intra-molecular H-bonding and proton transport in a series of acid-base complexes including different acid groups and nitrogenous heterocyclic rings were also studied by DFT calculations.²⁴⁻²⁵

In this work, DFT calculations will be applied to the characterization of proton transport in MI and its homologues, SI and PI, in terms of transition states and proton hopping. First, we will describe the DFT method in next section. And then, we will optimize the density functional and basis set in section 3.1, and will compare the intermolecular H-bonding energies in section 3.2. Third, we will study the transition states and energy barriers of proton transport mediated by water or EPA molecules as ethylene phosphonic acid is the most occurred repeat unit in PEMs. In addition, we also measured the overall conductivity of composites of MI and methyl phosphonic acid (MPA, the simplest organic phosphonic acid) at various compositions using electrochemical impedance spectroscopy (EIS). Finally, we will summarize the important results and propose that the MI and its homologues are building block candidates for the design of proton conducting polymers.

2. Methods

2.1 Calculation method

The generalized gradient approximation (GGA) functionals and hybrid functionals are

widely accepted in quantum chemistry because these functionals can provide reasonably accurate predictions for geometries and thermodynamics of small covalent molecules.²⁶⁻²⁸ However, the dispersion and H-bonding interactions are insufficiently represented by these functionals. In order to evaluate adequately the dispersion and H-bonding interactions, more accurate functionals, such as the meta-GGA functionals (the M06 family), dispersion corrected functionals (the B97-D), and long-range corrected functionals (the CAM-B3LYP), are developed.²⁹⁻³¹ Among the many physical and chemical processes, the proton transport is such a typical process which is greatly related to the weak intermolecular interactions, especially the H-bonding interaction. In order to evaluate their applicability to the proton transport in MI and its homologues, three functionals, including the hybrid B3LYP functional, the meta-GGA M06-2X functional and the counterpoise-corrected ω B97X-D functional, are compared in terms of intermolecular H-bonding interaction based on the MP2 reference. For these three functionals, the B3LYP is widely accepted for the calculation of organic molecules and considered being able to provide chemistry accuracy. The M06-2X and ω B97X-D functionals contain empirical dispersion corrections, especially suitable for the modeling of structures and energies of H-bonding interaction.³⁰ In addition, suitable basis set is selected from five basis sets including 6-311G(d), 6-311+G(d), 6-311+G(d,p), 6-311+G(2d,p), and 6-311++G(2d,2p). Based on the optimized functional and basis set, proton transport in molecular systems composed of MI, SI, PI, water, and EPA is studied in terms of geometric optimizations, frequency calculations, and transition state locations. Besides, the basis set superposition error (BSSE) are evaluated using counterpoise correction for energetics related to both intermolecular H-bonding and activation of proton transfer. The solvent effect is evaluated based on polarizable continuum model (PCM) using, respectively, water and phosphoric acid as solvents. The static

dielectric constant of phosphoric acid is assumed to be 18.90 by extrapolation of experimental dielectric constant of phosphoric acid solution as shown in **figure S3** in the supporting information.³² The optimized geometries are confirmed to be local minima without imaginary frequencies, or to be transition states with only one imaginary frequency. In addition, the reaction paths are traced by the internal reaction coordination (IRC) to ensure the correctness of the transition states. All the above calculations are conducted using the Gaussian 09 suite of programs.³³

2.2 Experimental method

The conductivities of the MI-based composites containing different amounts of MPA (Heowns Biochem Technologies Co. Ltd.) are characterized using electrochemical impedance spectroscopy (EIS). Firstly, the MI powders and MPA powders are mixed, ground, and pressed into round slabs ($\phi = 12.0$ mm, $t \approx 0.520$ mm) under a pressure of 14.0 Mpa. And then, the slabs are conditioned in a temperature and humidity controlled chamber (Boleda, model GDS-50) for 12 hours before each EIS measurement. Third, the EIS measurements are conducted using a multichannel potentiostat (Solartron, SI 1287) and a frequency response analyzer (Solartron, 1255B) by pressing the slabs between two round Pt electrodes. EIS are recorded in a frequency range from 1 Hz to 1 MHz with perturbation of 10.0 mV. The overall resistances of the slabs are obtained from the intercepts of the impedance spectra with the real axis at high frequencies, and the conductivities are evaluated from the overall resistances.

3. Results and discussion

3.1 Density functionals and basis sets optimization

The density functionals and basis sets are optimized according to the intermolecular

H-bonding interaction between two MI molecules as shown in **table 1**. The H-bonding energy is evaluated using three functionals including B3LYP, M06-2X, and ω B97X-D in combination with five basis sets of 6-311G(d), 6-311+G(d), 6-311+G(d,p), 6-311+G(2d,p), and 6-311++G(2d,2p) (be detailed in **table S1** of supporting information).

Table 1 Uncorrected and BSSE corrected H-bonding energies between two MI molecules evaluated using three functionals in combination with five basis sets, the values in parentheses are MP2 H-bonding energies evaluated using the corresponding DFT geometries (unit: kcal·mol⁻¹)

Basis set	B3LYP	B3LYP _{BSSE}	M06-2X	M06-2X _{BSSE}	ω B97X-D	ω B97X-D _{BSSE}
6-311G(d)	12.09	9.65	13.03	10.99	13.78	11.64
	(12.62)	(9.07)	(12.49)	(8.95)	(12.56)	(8.87)
6-311+G(d)	10.31	9.68	11.86	11.13	12.39	11.62
	(12.04)	(9.47)	(11.87)	(9.34)	(12.02)	(9.28)
6-311+G(d,p)	10.36	9.74	11.82	11.10	12.58	11.83
	(12.01)	(9.43)	(11.84)	(9.34)	(12.02)	(9.27)
6-311+G(2d,p)	10.05	9.61	11.22	10.73	12.33	11.79
	(12.41)	(10.41)	(12.37)	(10.39)	(12.45)	(10.34)
6-311++G(2d,2p)	10.04	9.60	11.30	10.81	12.33	11.81
	(12.84)	(10.56)	(12.82)	(10.55)	(12.93)	(10.50)

The H-bonding energy evaluated using B3LYP functional decreases with the size of basis sets from 12.09 to 10.04 kcal·mol⁻¹. Meanwhile the H-bonding energy calculated at MP2 level of theory and the corresponding geometries fluctuates between 12.01 and 12.84 kcal·mol⁻¹, with

a variation of $0.83 \text{ kcal}\cdot\text{mol}^{-1}$. And the average difference between the B3LYP functional and MP2 theory is about $-1.81 \text{ kcal}\cdot\text{mol}^{-1}$. That is to say, the H-bonding energy does not converge between the B3LYP functional and MP2 theory. For the M06-2X functional, the H-bonding energy converges to about $11.25 \text{ kcal}\cdot\text{mol}^{-1}$ as the basis set size increases, and the H-bonding energy evaluated using the MP2 theory increases from 11.84 to $12.82 \text{ kcal}\cdot\text{mol}^{-1}$ (the 6-311G(d) basis set is an outlier). In addition, the difference between the M06-2X functional and MP2 theory does not converge with a minimum difference of $-0.01 \text{ kcal}\cdot\text{mol}^{-1}$ and a maximum difference of $-1.52 \text{ kcal}\cdot\text{mol}^{-1}$. For the ω B97X-D functional, the H-bonding energy fluctuates between 12.33 to $13.78 \text{ kcal}\cdot\text{mol}^{-1}$, and converges at about $12.40 \text{ kcal}\cdot\text{mol}^{-1}$ as the basis set size increases, and the corresponding MP2 H-bonding energy fluctuates between 12.02 and $12.93 \text{ kcal}\cdot\text{mol}^{-1}$. The average difference between ω B97X-D functional and MP2 theory is only $0.29 \text{ kcal}\cdot\text{mol}^{-1}$.

After BSSE correction, all the H-bonding energies between two MI molecules are slightly decreased; however, their order does not change. As expected, the BSSE is more pronounced for small basis sets, which do not provide satisfactory description for wave functions farther from the nucleus, especially for the non-bonded interactions. Therefore, it could be concluded that the ω B97X-D functional provides the best H-bonding energy with the reference of MP2 theory, and the density functional theory always provides less H-bonding energy compared with the MP2 theory. Based on these calculations, the ω B97X-D functional will be applied to the following calculations in combination with the 6-311+G(2d,p) basis set.

Figure 1 summarizes the optimized structure of intermolecular H-bonding between two MI molecules based on the B3LYP/M06-2X/ ω B97X-D//6-311+G(2d,p) level of theory, as well as experimental values from crystal MI.³⁴ For the N-H $\cdots$ O bonding, the experimental distance

varies from 2.851 to 2.917 Å, and the theoretical value is from 2.880 to 2.919 Å, with the ω B97X-D//6-311+G(2d,p) in closest to the experimental values and the M06-2X//6-311+G(2d,p) the furthest. This is consistent with the fact that the ω B97X-D//6-311+G(2d,p) provides the strongest H-bonding interaction. For the C=O bond distances, the experimental values are in range of 1.190 to 1.221 Å, and the calculated values are between 1.197 to 1.204 Å, also in consistent with experimental values.

Fig. 1 Bond distances (Å) and angles (degree) between two MI molecules optimized using the B3LYP, M06-2X, and ω B97X-D functionals and 6-311+G(2d,p) basis set (color code: grey C, red O, cyan N, and purple H).

3.2 H-bonding energies of MI and its homologues

Though the imidic nitrogen ($>\text{N-H}$) is only bonded to three atoms leaving two nonbonding lone pair electrons, the imidic nitrogen could only behave as proton donor because it accepts a planar sp^2 hybridization attributing to the conjugation effect with two acyl (C=O) and one C=C double bonds. The imidic nitrogen is more difficult to be protonated (low basicity) than the amine nitrogen. On the other hand, the acyl oxygen could act as proton acceptor in H-bonding,

and thus, MI is an amphoteric compound. The proton affinity energies for acyl oxygen are -198.32, -203.69, and -206.37 kcal·mol⁻¹ for the MI, SI, and PI, respectively, evaluated at theory level of ω B97X-D/6-311+G(2d,p) as summarized in **table S2** in the supporting information. Therefore, the acyl oxygen atoms of MI show weaker proton affinity than those of SI and PI.

(a)

(b)

(c)

Fig. 2 (a) Maleimide MI and its homologues SI and PI; H-bonding between (b) two SI and (c) two PI molecules.

In this study, we also compare the H-bonding energies of MI with its homologues, SI and PI in which the C=C double bond is substituted, respectively, by a C–C single bond and a conjugated C=C double bond in a benzene ring as shown in **figure 2a**. The acidic dissociation constant (K_a) is a quantitative measure of the strength of an acid, and is related to the ionization degree of the acid in solution and thus the proton conductivity.³⁵ The logarithmic acidic dissociation constants (pK_a) of imidic protons (>N–H) of MI, PI, and SI are 5.57 (measured in this work as shown in **figure S1** of the supporting information), 9.90, and 9.62, respectively, with the imidic proton of MI the easiest to dissociate.³⁶ From the BSSE corrected intermolecular H-bonding energies as summarized in **table 2** (uncorrected H-bonding energies are detailed in **table S3** provided in the supporting information), it could be seen that these three homologues possess similar intermolecular H-bonding energies with the SI₂ at 12.59 kcal·mol^{−1} slightly greater than PI₂ at 12.10 kcal·mol^{−1} and MI₂ at 11.79 kcal·mol^{−1}, and the MI₂ the smallest. The N–H···O distances are 2.880, 2.862, and 2.876 Å, respectively, for MI₂, SI₂, and PI₂, also indicating the strongest H-bonding interaction in SI₂, the weakest in MI₂, and the intermediate in PI₂.

Table 2 H-bonding energies $-\Delta E$ (kcal·mol^{−1}) after BSSE correction and N–H···O distances d (Å) in MI₂, SI₂, and PI₂ evaluated using ω B97X-D functional in combination with five basis sets

Basis set	$-\Delta E_{\text{MI}}$	$-\Delta E_{\text{SI}}$	$-\Delta E_{\text{PI}}$	d_{MI}	d_{SI}	d_{PI}
6-311G(d)	11.64	12.30	11.91	2.893	2.881	2.892
6-311+G(d)	11.62	12.32	11.90	2.899	2.886	2.896
6-311+G(d,p)	11.83	12.61	12.12	2.885	2.870	2.881
6-311+G(2d,p)	11.79	12.59	12.10	2.880	2.862	2.876

6-311++G(2d,2p)	11.81	12.61	12.13	2.876	2.857	2.873
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The single-well potential or double-well potential with small barrier is an important characteristic of the intermediate complex for proton transfer in H-bonding. **Figure S2** shows the potential energy surfaces of proton transfer in MI₂, SI₂, and PI₂ systems. From **figure S2**, the distances of H-bonding which are susceptible to proton transfer processes are 2.341~2.391 Å for MI₂, 2.345~2.395 Å for SI₂, and 2.384~2.434 Å for PI₂. The activation energies of proton transfer are from 0.00 to 1.91 kcal·mol⁻¹ for MI₂, 0.12 to 3.70 kcal·mol⁻¹ for SI₂, 0.03 to 3.09 kcal·mol⁻¹ for PI₂, agreeing with the above H-bonding interaction energies.

3.3 Water mediated proton transfer between two MI molecules

In H-bonding, MI donates its imidic proton and accepts proton via acyl C=O, and resulting tautomerization interconversion between the keto and the enol forms and easing the fast proton transfer. For example, Kalia *et al.* calculated that the energy barrier for intramolecular tautomerization of MI is 56.97 kcal·mol⁻¹ in gaseous phase, and decreases to 23.52 kcal·mol⁻¹ mediated by one water molecule at B3LYP/6-31+G(d) level of theory.¹⁹ In solid state, two neighboring MI molecules are bound together via intermolecular N–H···O H-bonding and the imidic proton can hop between these two molecules. Such proton hopping process can be accelerated by water molecules or other amphoteric molecules existing between two MI molecules. In this section, we are going to evaluate the energy barriers of water mediated proton transfer in terms of intermolecular tautomerization.

(a)

(b)

Fig. 3 Tautomerization of MI mediated by (a) one, and (b) two water molecules, the unbolded numbers in parentheses are energies relative to the isolated molecules in gaseous phase and the bolded numbers are corresponding energies with solvation correction (color code: grey C, red O,

cyan N, and purple H).

In **figure 3**, it shows the water mediated proton transfer between two MI molecules including the initial states or reactants (Rea), transition states (TS), and products (Pro), as well as their energies relative to the isolated molecules in gaseous phase. For system $\text{MI}_2\text{-H}_2\text{O}$ (**figure 3a**), the water molecule mediates the proton transfer from imidic group (Rea1) to acyl group (Pro1) via a transition state TS1. In Rea1, the protons are bonded to imidic nitrogen atoms in either MI molecules with N–H distances at 1.023 and 1.029 Å, and $\text{O}\cdots\text{H}$ distances at 1.807 and 1.833 Å, respectively. In the TS1, the N–H distances are elongated to 1.362 and 1.483 Å, and the O–H distances are shortened to 1.139 and 1.159 Å. Finally in Pro1, both protons are transferred forming two lactim tautomers with O–H distances at 1.017 and 1.032 Å. All the intermolecular H-bonding distances are summarized in **table 3**. And solvation corrections are evaluated using of PCM solvation model of water based on the same geometries optimized at $\omega\text{B97X-D/6-311+G(2d,p)}$ level of theory. Energetically, Rea1 possesses a binding energy of $-20.07 \text{ kcal}\cdot\text{mol}^{-1}$ and the TS1 of $9.27 \text{ kcal}\cdot\text{mol}^{-1}$, which decreases to $-58.41 \text{ kcal}\cdot\text{mol}^{-1}$ and $-29.09 \text{ kcal}\cdot\text{mol}^{-1}$ after PCM solvation correction, respectively. Despite of the significance of PCM solvation correction to the total energies, the activation energy of water mediated proton transfer, the energy difference between TS1 and Rea1, is unaffected with values at $29.34 \text{ kcal}\cdot\text{mol}^{-1}$ or $29.32 \text{ kcal}\cdot\text{mol}^{-1}$ without or with solvation correction.

Table 3 Intermolecular H-bonding distances d (Å) in water and EPA mediated MI, SI, and PI systems evaluated at $\omega\text{B97X-D/6-311+G(2d,p)}$ level of theory

Rea	TS	Pro
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	$d_{\text{N-H}\cdots\text{O}}$	$d_{\text{O-H}\cdots\text{O}}$	$d_{\text{N-H}\cdots\text{O}}$	$d_{\text{O-H}\cdots\text{O}}$	$d_{\text{N-H}\cdots\text{O}}$	$d_{\text{O-H}\cdots\text{O}}$
MI ₂ -H ₂ O	2.847,	2.781	2.482,	2.391	2.665,	2.504
	2.794		2.538		2.675	
MI ₂ -2H ₂ O	2.772,	2.783,	2.539,	2.413,	2.774,	2.523,
	2.772	2.783	2.539	2.413	2.774	2.523
MI-EPA	2.759	2.672	2.479	2.406	2.636	2.508
MI ₂ -EPA	2.743	2.735,	2.554	2.392,	2.663	2.463,
		2.738		2.688		2.712
SI ₂ -H ₂ O	2.839,	2.755	2.475,	2.387	2.727,	2.524
	2.787		2.524		2.690	
SI ₂ -2H ₂ O	2.746,	2.788,	2.506,	2.444,	2.817,	2.537,
	2.746	2.788	2.506	2.444	2.817	2.537
SI-EPA	2.761	2.650	2.475	2.412	2.656	2.529
SI ₂ -EPA	2.779	2.683,	2.531	2.392,	2.701	2.486,
		2.723		2.652		2.682
PI ₂ -H ₂ O	2.859,	2.767	2.473,	2.395	2.675,	2.511
	2.793		2.544		2.681	
PI ₂ -2H ₂ O	2.753,	2.803,	2.535,	2.417,	2.780,	2.525,
	2.753	2.803	2.535	2.417	2.780	2.525
PI-EPA	2.761	2.668	2.480	2.411	2.638	2.512
PI ₂ -EPA	2.746	2.715,	2.549	2.391,	2.668	2.469,
		2.760		2.708		2.731

The system MI₂-2H₂O (**figure 3b**) shows the proton transfer between two MI molecules mediated by two water molecules. The bond lengths of N–H and O··H in Rea2 are similar to that of Rea1, while for the TS2, one of the N–H bond is elongated to 1.539 Å, and O–H shortened to 1.286 Å. For the product Pro2, two of the imidic protons are transferred becoming two lactim protons, with N··H distances being elongated to 1.869 Å and O–H distances being shortened to 1.031 Å. The proton transfer barrier is 29.90 kcal·mol^{−1} without PCM solvation correction, almost the same as that with one mediation water molecule, slightly different from those with PCM solvation correction (**table 4**).

Table 4 BSSE corrected energetics (kcal·mol^{−1}) related to the proton transfer in MI and the values in parentheses are corresponding energetics with PCM solvation correction[†]

Energy	MI ₂ -H ₂ O	MI ₂ -2H ₂ O	MI-EPA	MI ₂ -EPA	MI-H ₂ O [‡]
Rea	-20.07	-29.02	-16.97	-32.05	0.00
	(-58.41)	(-78.36)	(-62.24)	(-88.99)	
TS	9.27	0.88	-3.35	-18.36	23.52
	(-29.09)	(-46.49)	(-49.37)	(-75.43)	
Pro	7.36	-4.58	-4.93	-19.24	17.63
	(-30.43)	(-51.33)	(-50.38)	(-76.17)	
ΔE_a	29.79	29.90	13.62	13.69	23.52
	(29.32)	(31.87)	(12.88)	(13.56)	

[†] relative to isolated molecules in gaseous phase evaluated at ω B97X-D/6-311+G(2d,p) level of theory

[‡] relative to the stable state of MI-H₂O complex evaluated at B3LYP/6-31+G(d) level of theory¹⁹

3.4 EPA mediated proton transfer between two MI molecules

From previous section, it is concluded that proton transfer occurs between two MI molecules mediated by water molecules because of the amphoteric characteristics of MI. In this section, we are going to study the EPA mediated proton transfer between two MI molecules since phosphonic acid is considered a potential substitution to the sulfonic acid based proton exchange membranes. And solvation corrections are evaluated using of PCM solvation model of phosphoric acid based on the same geometries optimized at ω B97X-D/6-311+G(2d,p) level of theory.

Table 4 reveals that solvation greatly lowers the total energies, however, the activation energies of proton transfer almost conserve. In **figure 4**, it shows the tautomerization of MI mediated by EPA molecule (molar ratio=1:1). In **figure 4a**, a MI molecule tautomerizes from a lactam structure to a lactim structure with an energy barrier of only 12.88 kcal·mol⁻¹ corrected with PCM solvation model in phosphoric acid, which is comparable to the experimental activation energy for phosphonic acid functionalized polyimide composite membranes.³⁷ It is well known that the proton conductivity depends on the content of phosphonic acid.³⁸ From **figure 4b** which shows the tautomerization in a system consisting of two MI molecules and one EPA molecule, it could be seen that an EPA could form triple fold H-bonding linkages between two MI molecules functioning simultaneously as H-bonding donor and acceptor. The proton transfer barrier between MI and EPA is 13.56 kcal·mol⁻¹, a little more than the energy barrier 12.88 kcal·mol⁻¹ and less than half of that between two MI molecules mediated by one or two water molecules. Therefore, it could be expected that MI will potentially improve the proton conductivity in EPA, and MI is a candidate solvation media for phosphonic acid based proton exchange membranes.

(a)

(b)

Fig. 4 Tautomerization of (a) MI mediated by EPA, (b) two MI molecules mediated by EPA, the unbolded numbers in parentheses are energies relative to the isolated molecules in gaseous phase and the bolded numbers are corresponding energies with solvation correction (color code:

grey C, red O, cyan N, purple H, and yellow P).

Figure 5 shows the overall conductivity of the MI-MPA composite at various compositions $\text{MI}_{1-x}\text{MPA}_x$ measured at 45 °C and 40% RH. Notice that the measurement for the pure MPA slab fails as MPA is sensitive to moisture and easily deliquesces, and the overall conductivity of the pure MI slabs at 40% RH is below detecting limit. The overall characteristics of conductivity is comparable with that of the phosphonic acid and triazolyl functionalized polystyrene, where synergetic proton conduction is observed attributing to the interaction between the phosphonic acid group and the 1,2,3-triazolyl group.¹³ Though pure MPA possesses low conductivity, its conductivity greatly increases as more and more MI is composited into MPA. In MI-MPA composite composing of 0.663 MPA (MPA : MI $\approx$ 2 : 1), a maximum overall conductivity is observed at 1.87 mS cm⁻¹ also comparable to that of the phosphonic acid and triazolyl functionalized polystyrene.¹³ As more MI is composited, the overall conductivity decreases. Therefore, it is concluded that the MI can be applied as additive to improve the conductivity of phosphonic acid based proton conducting materials, and MI can be used as novel building block for the design of proton conducting materials.

Fig. 5 Overall conductivity of the MI-MPA composite measured at 45 °C and 40% RH (The connecting lines are guide to the eyes.)

3.5 Water and EPA mediated proton transfer between the MI homologues

In previous sections, we discussed the possibility of MI as candidate building block for proton exchange membranes. In this section, we are going to evaluate the characteristics of two of its homologues of MI, including SI and PI. **Figures 6 and 7** show the proton transfer pathways between two SI molecules and two PI molecules mediated by water and EPA, respectively. The energetics related to the proton transfer in SI and PI are summarized in **table 5**.

3.5.1 Water and EPA mediated proton transfer between two SI molecules

Differing from MI and PI, where we cannot localize any transition states for direct tautomerization without mediation molecules, we localize a transition state for direct tautomerization between two SI molecules without any mediation molecules as shown in **figure**

6a. During direct tautomerization of two SI molecules, the N–H distance increases from 1.027 (Rea5) to 1.410 (TS5), and finally to 1.572 Å (Pro5), meanwhile, the O–H distance decreases from 1.851, to 1.107, and to 1.038 Å. In addition, tautomerization could also be mediated by water molecules and EPA molecules as shown in **figures 6b–6e**. From the typical energetics (**table 5**), the activation energy without any mediation molecules is 21.55 kcal·mol^{−1}, and this energy increases to 26.86 and 28.39 kcal·mol^{−1} if the tautomerization is mediated by one or two water molecules with correction of PCM solvation model of water. These values are comparable with activation energies for intramolecular tautomerization of SI. For example, the activation energies for intramolecular keto-enol tautomerization of SI are 19.12 and 16.11 kcal·mol^{−1} with one and two water molecules, respectively, evaluated at theory level of MP2/6-311++G(d,p).³⁹ In addition, the activation energies for water assisted enol-keto tautomerization of *N*-methylacetamide are also reported to be at slightly above 20.0 kcal·mol^{−1}.⁴⁰

In our previous study, it was found that the phosphonic acid could greatly accelerate the tautomerization of 1,2,3-triazole by reduction of activation energy from about 1.0 eV to about 0.35 eV.²² In this study, it is found that the activation energy of SI mediated by EPA molecule decreases to 11.26 kcal·mol^{−1} with correction of PCM solvation model of phosphoric acid, consistent with MI and 1,2,3-triazole.

(a)

(b)

(c)

(d)

Fig. 6 Tautomerization of (a) two SI molecules, two SI molecules mediated by (b) one, and (c) two water molecules, (d) one SI, and (e) two SI molecules mediated by EPA, the unbolded numbers in parentheses are energies relative to the isolated molecules in gaseous phase and the bolded numbers are corresponding energies with solvation correction (color code: grey C, red O, cyan N, and purple H).

3.5.2 Water and EPA mediated proton transfer between two PI molecules

Figure 7 summarizes the proton transfer pathways between two PI molecules with the mediation of water molecules or EPA molecules. The structural parameters, the N–H and O···H distances, are similar to those of the MI systems. The activation energies also show similar values and tendency compared with those of MI systems, and are lower than that of PBI- x H₃PO₄ system (17.2~20.2 kcal·mol⁻¹).⁴¹ From **table 5**, it is obvious that activation energies for the

keto to enol tautomerization are higher than that for the backward enol to keto activation, in consistent with literature.⁴²

(a)

(b)

Fig. 7 Tautomerization of two PI molecules mediated by (a) one, and (b) two water molecules, and (c) one PI, and (d) two PI molecules mediated by EPA, the unbolded numbers in parentheses are energies relative to the isolated molecules in gaseous phase and the bolded numbers are

corresponding energies with solvation correction (color code: grey C, red O, cyan N, and purple H).

Table 5 BSSE corrected energetics ($\text{kcal}\cdot\text{mol}^{-1}$) related to the proton transfer in SI and PI systems and the values in parentheses are energetics with PCM solvation correction

	Rea	TS	Pro	$\Delta E_a^\ddagger$	$\Delta E_a^\ddagger$
SI ₂	-12.59	9.08	8.59	21.67	0.49
	(-41.59)	(-20.04)	(-20.16)	(21.55)	(0.12)
SI ₂ -H ₂ O	-20.79	6.43	2.29	27.22	4.14
	(-61.18)	(-34.32)	(-37.27)	(26.86)	(2.95)
SI ₂ -2H ₂ O	-30.63	-3.77	-11.55	29.05	7.78
	(-80.65)	(-52.27)	(-59.66)	(28.39)	(7.39)
SI-EPA	-17.55	-5.33	-7.41	12.21	2.08
	(-64.01)	(-52.75)	(-54.04)	(11.26)	(1.30)
SI ₂ -EPA	-34.60	-22.06	-22.07	12.53	0.01
	(-93.13)	(-80.83)	(-82.54)	(12.30)	(1.71)
PI ₂ -H ₂ O	-20.21	9.65	7.08	29.87	2.57
	(-67.42)	(-38.24)	(-39.69)	(29.18)	(1.44)
PI ₂ -2H ₂ O	-29.56	0.15	-5.54	29.71	5.69
	(-86.64)	(-56.20)	(-61.30)	(30.44)	(5.10)
PI-EPA	-17.07	-3.64	-5.21	13.43	1.57
	(-66.85)	(-54.24)	(-55.31)	(12.61)	(1.07)
PI ₂ -EPA	-33.77	-20.21	-21.23	13.55	1.02

(-99.81) (-86.48) (-87.36) (13.33) (0.88)

[†] activation energy for keto to enol tautomerization

[‡] activation energy for enol to keto tautomerization

4. Conclusions

DFT calculations are applied to the investigation of H-bonding characteristics in MI, SI, and PI in terms transition states at theory level of ω B97X-D/6-311+G(2d,p). The intermolecular H-bonding energies are evaluated at 11.79, 12.59, and 12.10 kcal·mol⁻¹ for the MI, SI, and PI dimers with BSSE correction, respectively, indicating their similarity in H-bonding as the maximum difference in H-bonding energy is only 0.29 kcal·mol⁻¹. The proton transfer barrier between two MI molecules mediated by water molecules is about 30.60 kcal·mol⁻¹ calculated in terms of transition state, and can be lowered further to about 13.22 kcal·mol⁻¹ mediated by EPA molecules (with PCM solvation model correction). From these calculations, it is concluded that proton transfer between MI molecules are efficient and can be improved by EPA mediation molecules. In addition, the homologues of MI, SI and PI, possess similar characteristics in H-bonding and proton transfer compared with MI.

From these characteristics, it is concluded that MI and its homologues possess the essential properties for intermolecular proton transport, and therefore, we propose that the MI and its homologues are building block candidates for the design of proton conducting polymers.

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