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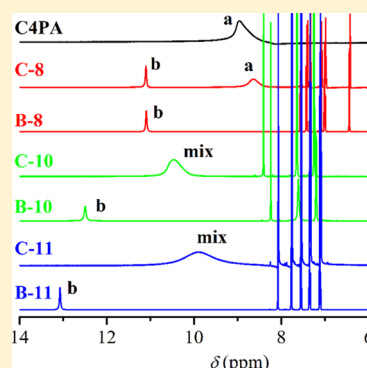
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Hydrogen Bond and Proton Transport in Acid–Base Complexes and Amphoteric Molecules by Density Functional Theory Calculations and ^1H and ^{31}P Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Intermolecular and intramolecular hydrogen bond (H-bond) and proton transport in acid–base complexes and amphoteric molecules consisting of phosphonic acid groups and nitrogenous heterocyclic rings are investigated by density functional theory calculations and ^1H NMR and ^{31}P NMR spectroscopy. It is concluded that a phosphonic acid group can act both as H-bond donor and H-bond acceptor, while an imine nitrogen atom can only act as H-bond acceptor and an amine group as H-bond donor. And the intramolecular H-bond is weaker than the intermolecular H-bond attributing to configurational restriction. In addition, the strongest H-bond interaction is observed between a phosphonic acid and a 1*H*-indazole because of the formation of double H-bonds. The ^1H NMR and ^{31}P NMR chemical shifts for the acid–base complexes are consistent with the density functional theory calculations. From the ^1H NMR chemical shifts, fast proton exchange is observed between a phosphonic acid and 1*H*-benzimidazole or 1*H*-indazole. Finally, it is proposed that polymeric material tethered with 1*H*-benzimidazole or 1*H*-indazole rings is a favorable component for high-temperature proton exchange membranes based on acid–base complexes or acid–base amphoteric molecules.



1. INTRODUCTION

The sustainable development of modern economy and modern society depends not only on the exploitation of reusable energy resources but also on the innovation and improvement of energy conversion devices. Owing to their high energy conversion efficiency, environmental friendliness, and structural compactness, proton exchange membrane fuel cells (PEMFCs) have attracted more and more attention both from academic institutions and commercial organizations.^{1,2} As one of the two essential materials of PEMFCs and direct methanol fuel cells (DMFCs), proton exchange membrane (PEM) serves as a separator between anodic and cathodic chambers, proton conductor offering selective ionic and molecular transport channels, and substrate for the loading of electrocatalysts. However, the proton conductivity of the most widely accepted PEMs based on poly(perfluorosulfonic acid) or other sulfonated polymers, e.g., NAFION, seriously degrades from evaporation dehydration at high temperature.³ Therefore, it is difficult to apply such PEMs to the intermediate to high-temperature (120–200 °C) PEMFCs operated at temperatures well above the boiling point of water.^{4–10} High operational temperature is expected for PEMFCs attributing to their high energy conversion efficiency, simplified water and heat management systems, low Pt-loading on electrocatalysts because of the enhancement of catalytic activity at high temperatures, and high CO tolerance in feed-gas.^{4,11,12}

Among the many high-temperature proton exchange membranes (HT-PEMs), PEMs based on polymeric acid–base complexes or acid–base amphoteric polymers and copolymers are promising owing to their high proton

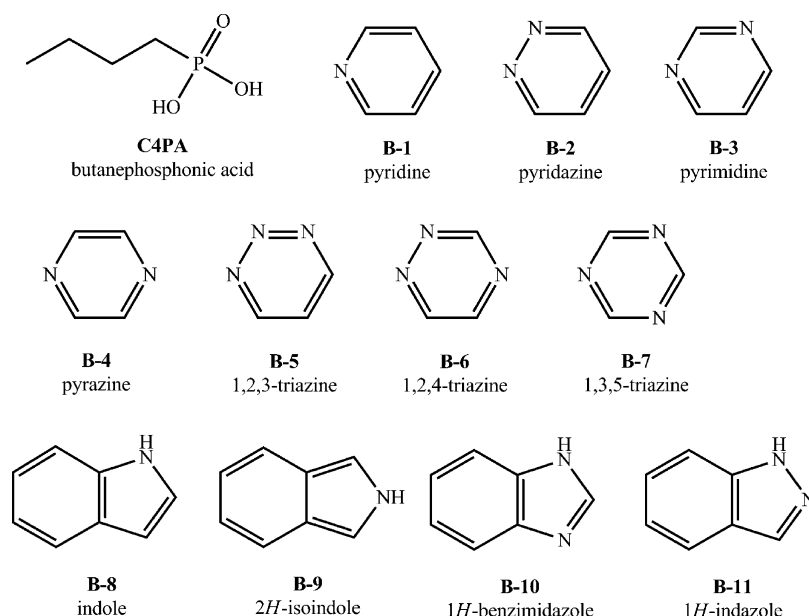
conductivity in dehydrated state at high temperatures.¹³ For example, the copolymer based on vinylphosphonic acid (VPA) and 1-vinyl-1,2,4-triazole (VTri) shows proton conductivity of 1 $\text{mS}\cdot\text{cm}^{-1}$ at 120 °C far higher than the imidazole based copolymers in the absence of humidity, and is a promising candidate of HT-PEM.¹⁴ The ionically cross-linked poly(vinylphosphonic acid)–poly(1-vinyl-1,2,4-triazole) complex possesses a proton conductivity of 2.5 $\mu\text{S}\cdot\text{cm}^{-1}$ at 180 °C in the anhydrous state, and 8–22 $\text{mS}\cdot\text{cm}^{-1}$ after humidification at 100 °C closing to the NAFION 117 at the same humidity level.¹⁵ The sulfonated poly(ether ether ketone) (SPEEK) incorporated with imidazole microcapsules exhibits an ultralow proton conductivity decline at relative humidity as low as 20%, and the proton conductivity is 1–2 orders of magnitude higher than that of the sulfonated SPEEK membrane without dopant.¹⁶ However, the proton conductivities of poly(vinylbenzyl phosphonic acid-statistical-4-vinyl pyridine)s are quite low at 150 °C and exhibit time-dependent changes due to the formation of anhydride at elevated temperatures.¹⁷ Therefore, the performances of HT-PEMs based on acid–base complexes or acid–base amphoteric polymers and copolymers depend on the elaborated design of the molecular structure, especially the selection of acidic functional groups and basic functional groups.^{18,19} Some of the other acid–base high-temperature proton exchange materials include polymers and copolymers functionalized with triazole groups,^{20,21}

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Scheme 1. The Model Molecules



sulfonated poly(arylene ethers) containing azole groups,²² carboxylic acid functional triazole,²³ phosphonic acids,²⁴ triazole and triazole derivatives,²⁵ imidazole-like dimers containing imidazole, triazole, and tetrazole.^{14,26}

In the design and preparation of HT-PEMs based on acid–base complexes or amphoteric polymers and copolymers, the acidic functional groups could only be selected from a few functional groups including the sulfonic acid group, phosphonic acid group, and carboxylic acid group; however, the basic functional groups could be selected from a great diversity of nitrogenous heterocyclic groups such as imidazolyl, pyrazolyl, benzimidazolyl, triazolyl, etc. In the early development of HT-PEMs, the nitrogenous bases such as imidazole,²⁷ triazole,^{28,29} pyrazole,³⁰ and pyrrole¹⁸ were employed to substitute water at high temperature for the solvation of the sulfonic acid group owing to their high boiling temperature and low vapor pressure. In addition, these nitrogenous heterocycles are all self-dissociable amphoteric nitrogenous bases showing relatively high conductivities at high temperatures.³¹ In fact, the nitrogenous heterocycles are versatile components in the formation of a hydrogen bond (H-bond) network, which is an essential structural motif for the proton transport, in the acid–base complexes or amphoteric polymers and copolymers as revealed by density functional theory calculations as well as ¹H NMR spectroscopy and MAS ¹H NMR spectroscopy.^{18,31–33} Recently, the HT-PEM based on heterocyclic protogenic solvents including imidazole, benzimidazole, pyrazole, triazole, and tetrazole was reviewed.¹³

In order to design and develop better HT-PEMs, much efforts are also devoted to the understanding of proton transport mechanisms. In the acid–base complexes or amphoteric polymers and copolymers, protons hop from H-bond donors to H-bond acceptors in the H-bond network without the macroscopic transport of any vehicular molecules or groups. This hopping mechanism is also known as structural diffusion or the non-vehicular mechanism in contrast to the vehicular mechanism in the hydrated sulfonic acid systems.³⁴ The structural diffusion is facilitated by the formation and rearrangement of pervasive H-bond network, as well as the

formation of charge defects in terms of excess or missing protons.^{27,30,34–38} Therefore, a fundamental understanding of inter- and intramolecular H-bond interaction can provide important information for the design of HT-PEMs based on acid–base complexes or amphoteric polymers and copolymers.^{39,40}

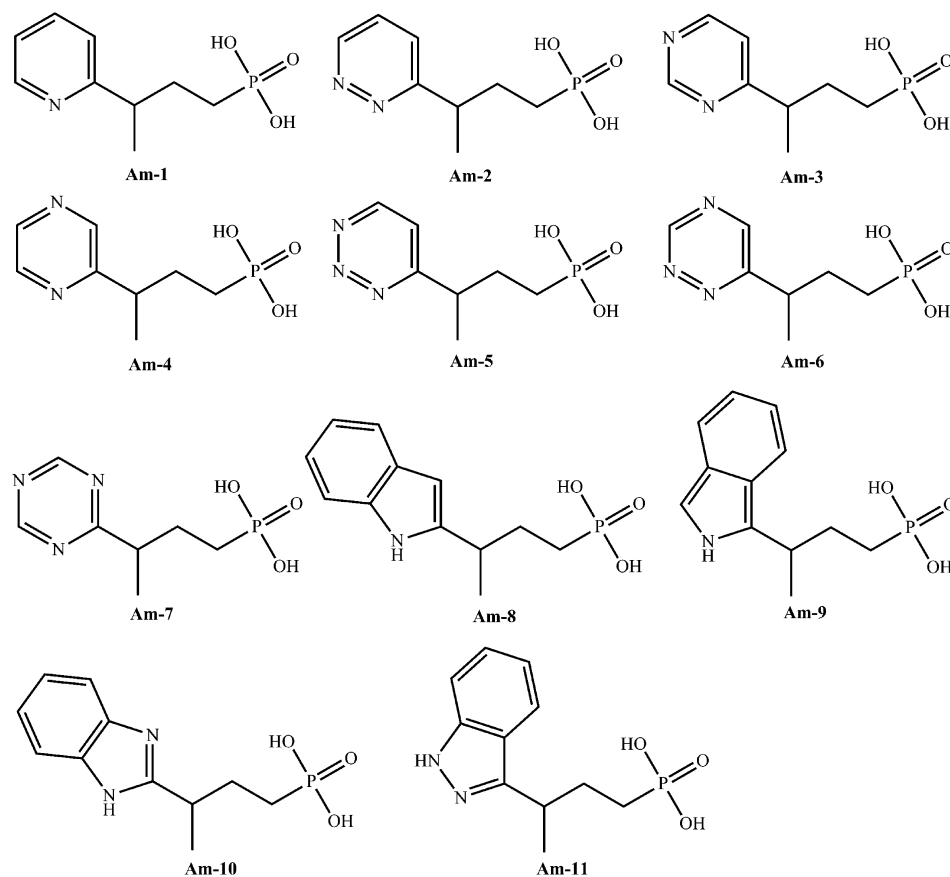
The H-bond interaction and H-bond network could be studied by experimental observations or theoretical calculations. For example, Suarez et al. studied the proton transport in phosphoric acid doped poly(benzimidazole) by use of ¹H and ³¹P NMR spectra,⁴¹ and Brunklaus et al. concluded that there is no simple connection between H-bond strength, local mobility, and efficient bulk proton conductivity in systems consisting of phosphonic acid based on solid state NMR observations.³⁶ Zhang and Yan et al. studied the proton transport mechanism by density functional theory calculations of model molecular systems, as well as ¹H NMR spectroscopy.^{18,19,32}

In this study, we are going to investigate the inter- and intramolecular H-bond interaction between phosphonic acid groups and nitrogenous heterocyclic groups using density functional theory calculations of model acid–base complexes and amphoteric molecules. In addition, ¹H NMR and ³¹P NMR spectroscopy will also be applied to the characterization of H-bond characteristics of acid–base complexes and amphoteric molecules to verify the density functional theory calculation results. Finally, the proton transport characteristics will be discussed in terms of density functional theory calculations and ¹H NMR and ³¹P NMR spectroscopy.

2. METHODS

2.1. Model Molecules and Molecular Systems. In order to study the H-bond interaction between a phosphonic acid group and a nitrogenous heterocyclic group, two types of model systems including the acid–base complexes and acid–base amphoteric molecules were studied. The acid–base complexes (C-1 to C-11), which are composed of a butanephosphonic acid (C4PA) and a nitrogenous heterocyclic base (B-1 to B-11) (Scheme 1), are model systems of intermolecular H-bond interaction, and the acid–base ampho-

Scheme 2. The Model Acid–Base Amphoteric Molecules



teric molecules (**Am-1** to **Am-11**), which consist of a phosphonic acid group and a nitrogenous heterocyclic group, which corresponds to the nitrogenous heterocyclic base of **B-1** to **B-11**, in the same molecule (Scheme 2), are model systems of intramolecular H-bond interaction.

The nitrogenous heterocyclic bases are composed of one 6-membered ring with one to three nitrogen atoms, or a fused benzene ring and 5-membered ring with one or two nitrogen atoms. These nitrogenous heterocyclic moieties are representatives of various basic ingredients which could be widely found in HT-PEMs as heterocyclic solvents and basic polymers and copolymers. The acid–base amphoteric molecules are also representatives of various acid–base amphoteric polymers and copolymers, as well as functionalized polymers with both phosphonic acid group and heterocyclic base group. Therefore, the H-bond and proton transport characteristics revealed from these model systems are representative of the relevant acid–base complexes or acid–base amphoteric polymers and copolymers for HT-PEMs.

2.2. Computational Details. All the calculations were carried out on the basis of density functional theory and single point second-order Möller–Plesset (MP2) perturbation theory as implemented in the Gaussian 03 package.⁴² First, all the molecular systems including the acid and base molecules, the acid–base complexes, and acid–base amphoteric molecules were optimized at the B3LYP/6-311+G(2d,p) level of theory. And then, vibrational frequency calculations were conducted to verify if local minima had reached (with or without imaginary frequencies). The optimizations were satisfactory, since local minima were achieved for all the molecular systems. Finally, for higher accuracy in terms of energetics, single point calculations

were performed at the MP2/6-311+G(2d,p) level of theory for all the optimized molecular systems.

2.3. H-Bond Energy. The intermolecular H-bond energy of an acid–base complex was calculated as the energy difference between the complex and the isolated acid and base molecules^{43,44}

$$\Delta E_{\text{HB}}^{\text{inter}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} + \text{ZPE} \quad (1)$$

where $\Delta E_{\text{HB}}^{\text{inter}}$ is the intermolecular H-bond energy, E_{AB} , E_{A} , and E_{B} are the total energies of the acid–base complex, the isolated acid, and base molecules, respectively, and ZPE is the zero point energy correction evaluated during the frequency calculations. The intermolecular H-bond energy is further corrected by the basis set superposition error (BSSE) based on the counterpoise procedure^{45,46}

$$\Delta E_{\text{HB,c}}^{\text{inter}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} + \text{ZPE} + \text{BSSE} \quad (2)$$

The intramolecular H-bond energy was evaluated as the energy difference between two conformations of the same amphoteric molecule

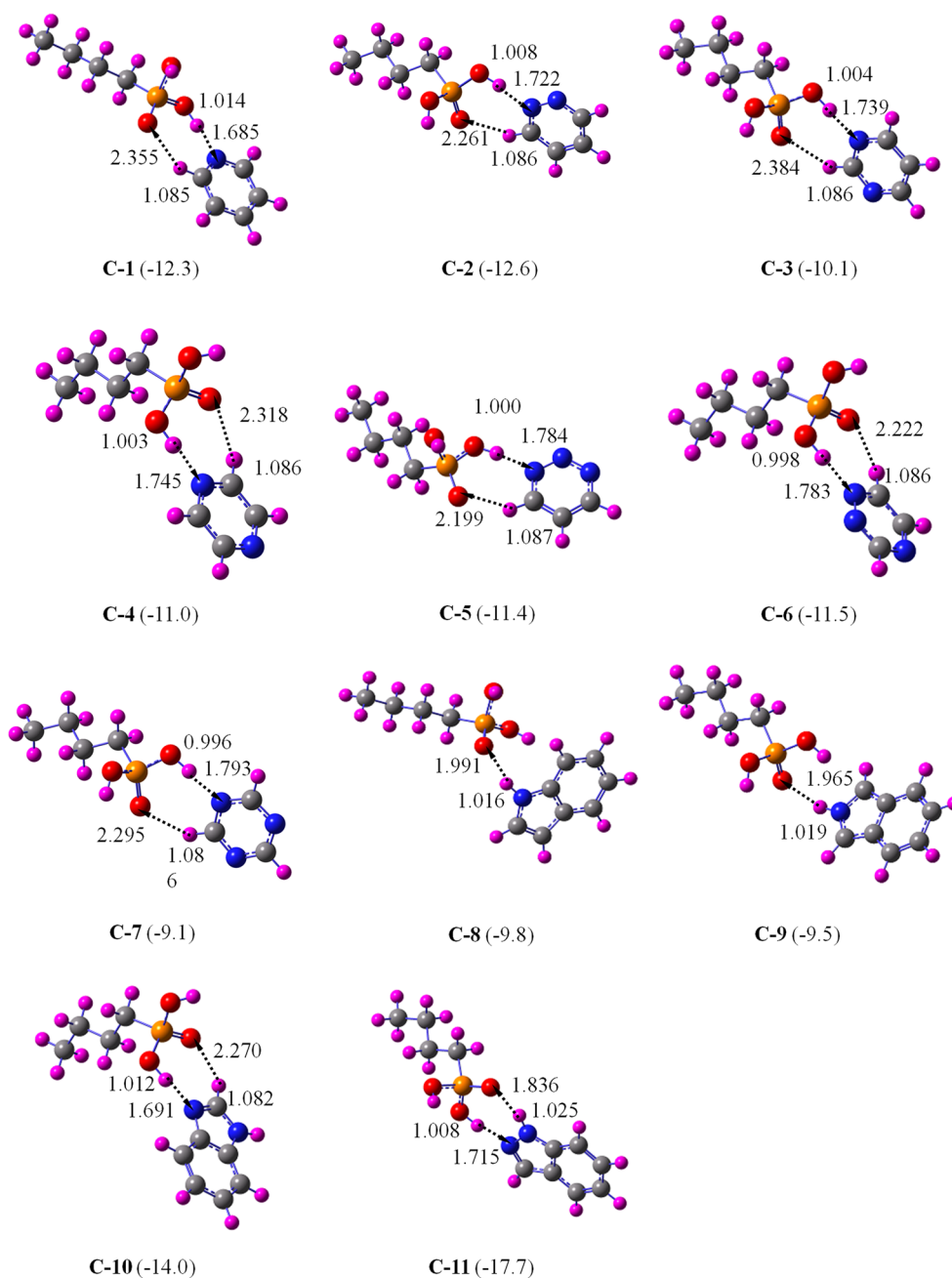
$$\Delta E_{\text{HB}}^{\text{intra}} = E_{\text{HBnd}} - E_{\text{NHBnd}} + \text{ZPE} \quad (3)$$

where $\Delta E_{\text{HB}}^{\text{intra}}$ is the intramolecular H-bond energy, E_{HBnd} and E_{NHBnd} are the total energies of the acid–base amphoteric molecule with or without H-bond interaction, respectively, and ZPE is the zero point energy correction evaluated during the frequency calculations.

2.4. ¹H NMR and ³¹P NMR Measurements. ¹H NMR and ³¹P NMR measurements were used to characterize the H-bond interaction. The ¹H NMR spectra were recorded on a Bruker

Table 1. Comparison of H-Bond Energy $\Delta E_{\text{HB,c}}$ of the C4PA–Pyridine Complex (C-1) Evaluated at Various Levels of Theory (Units: kcal mol^{−1})^a

	B3LYP	PBE1PBE	B3PW91	MPW1PW91
6-31G(d)	−13.4 (−16.5)	−14.4 (−16.5)	−12.6 (−16.6)	−13.6 (−16.5)
6-311+G(d,p)	−11.8 (−15.4)	−13.5 (−15.4)	−11.7 (−15.4)	−12.6 (−15.4)
6-311+G(2d,p)	−11.2 (−15.7)	−12.7 (−15.7)	−11.0 (−15.7)	−11.9 (−15.8)
6-311++G(2d,2p)	−11.1 (−15.9)	−12.6 (−15.9)	−10.9 (−15.9)	−11.8 (−15.9)

^aThe numbers in parentheses are MP2 energies of the same geometries calculated using the corresponding basis set.**Figure 1.** Inter-molecular H-bond and bonding energies (numbers in parentheses in kcal·mol^{−1}) in acid–base complexes evaluated at the B3LYP/6-311+G(2d,p)//MP2/6-311+G(2d,p) level of theory.

AV 500 MHz spectrometer with a ¹H resolution of 0.45 Hz and tetramethylsilane (TMS) as internal reference, and ³¹P NMR spectra were recorded on a Varian 400 MHz spectrometer with

a ³¹P resolution of 2.47 Hz and 85% H₃PO₄ as external reference. The samples were kept at 22 °C for the NMR experiments except for the temperature dependent experiments

Table 2. Intermolecular H-Bond Parameters for the Acid–Base Complexes

system	$d_{\text{N(C)}-\text{H}}$ (Å)	$d_{\text{O}-\text{H}}$ (Å)	$\angle\text{N(C)HO}$ (deg)	ν (cm ^{−1})	$\Delta E_{\text{HB}}^{\text{inter}}$ (kcal mol ^{−1})	$\Delta E_{\text{HB,C}}^{\text{inter}}$ (kcal mol ^{−1})
C-1	1.685	1.014	176.7	2865	−13.0	−12.3
	1.085	2.355	141.8	3162		
C-2	1.722	1.008	173.2	2980	−13.2	−12.6
	1.086	2.261	143.2	3161		
C-3	1.739	1.004	177.0	3056	−10.7	−10.1
	1.086	2.384	140.0	3176		
C-4	1.745	1.003	175.4	3067	−11.6	−11.0
	1.086	2.318	141.4	3160		
C-5	1.784	1.000	171.3	3169	−12.1	−11.4
	1.087	2.199	143.4	3152		
C-6	1.783	0.998	171.9	3167	−12.1	−11.5
	1.086	2.222	142.5	3154		
C-7	1.973	0.996	175.1	3204	−9.7	−9.1
	1.086	2.295	140.2	3171		
C-8	1.016	1.969	151.8	3497	−10.6	−9.8
C-9	1.019	1.965	148.3	3462	−10.2	−9.5
C-10	1.691	1.012	173.0	2905	−14.7	−14.0
	1.082	2.270	134.2	3218		
C-11	1.025	1.836	152.2	3343	−18.5	−17.7
	1.715	1.008	171.1	2972		

where the temperatures were specified as the NMR results were reported. The NMR spectra were recorded in solvent of DMSO- d_6 (99.9%, containing 0.03% v/v TMS, the Cambridge Isotope Laboratories, Inc.) or in tetrahydrofuran- d_8 (THF- d_8 , 99.5%, the Cambridge Isotope Laboratories, Inc.) in the temperature dependent experiments. The **C4PA** (98%) was supplied by Alfa Inc., pyrimidine (**B-3**, 97%) and 1*H*-benzimidazole (**B-10**, 99%) were supplied by the Aladdin Inc., pyridine (**B-1**) was supplied by Sinopharm Inc., 1*H*-indazole (**B-11**, 99%), pyridazine (**B-2**, 98%), pyrazine (**B-4**, 99%), and indole (**B-8**, 99%) were supplied by Adamas Inc., and 1,3,5-triazine (**B-7**, 98%) was supplied by TCI Inc.. All the chemicals were used as received without further purification but were degassed by freeze–pump–thaw cycles before use. And for all the acid–base complexes, their molar ratio of acid to base is 1:1.

3. RESULTS AND DISCUSSION

3.1. Method and Basis Set Selection. In order to screen out the suitable functionals and basis sets, the complex of **C4PA**–pyridine (**C-1**) was studied in terms of H-bond energy using various functionals and basis sets. Four functionals including B3LYP, PBE1PBE, B3PW91, and MPW1PW91 and four basis sets including 6-31G(d), 6-311+G(d,p), 6-311+G(2d,p), and 6-311++G(2d, 2p) were compared. In addition, MP2 calculations were also performed to obtain accurate reference energies based on the optimized geometries using density functional theory calculations.

From the H-bond energy calculated at various levels of theory as summarized in Table 1, it could be concluded that the 6-31G(d) and 6-311+G(d,p) basis sets do not provide converged H-bond energies with any functionals. From the basis set 6-31G(d) to 6-311+G(d,p), an about 1.1 kcal mol^{−1} decrease in H-bond energy was observed. If a larger basis set 6-311+G(2d,p) was used, the H-bond energy further decreased by about 0.7 kcal mol^{−1}. However, if we go from basis set 6-311+G(2d,p) to 6-311++G(2d, 2p), only about 0.1 kcal mol^{−1} decrease in H-bond energy was observed. Therefore, it was concluded that the 6-311+G(2d,p) basis set provides

comprehensive performance if both calculation accuracy and efficiency were considered.

From the H-bond energies evaluated using MP2 based on the same basis set but geometries optimized using different functionals, almost the same H-bond energies were obtained for all functionals with the same basis set. Thus, it was concluded that these functionals provide similar geometries for all the systems without significant differences. Considering that the hybrid B3LYP functionals have achieved the greatest success in terms of the number of published applications⁴⁷ and are still among the best functionals that provide accurate predictions for geometries and thermochemistry of small covalent molecules, the hybrid B3LYP functionals will be used in the following calculations to obtain geometries of the isolated molecules and molecular systems. In addition, MP2 calculations were conducted to obtain the total energy using the 6-311+G(2d,p) basis set based on geometries optimized using the B3LYP functionals.

3.2. Intermolecular H-Bond. The H-bond structures and parameters of the acid–base complexes calculated at the B3LYP/6-311+G(2d,p)//MP2/6-311+G(2d,p) level of theory were summarized in Figure 1 and Table 2. From Figure 1, it could be concluded that there are two types of H-bonds formed in the acid–base complexes including the N···H–O bond and O–H···N bond. The phosphonic acid group could act both as H-bond acceptor and donor, while the secondary heterocyclic amine group could only act as H-bond donor and heterocyclic imine nitrogen atom as H-bond acceptor. The strongest H-bond with a H-bond energy at −17.7 kcal·mol^{−1} is formed in the complex of 1*H*-indazole (**B-11**) and **C4PA**, as both **C4PA** and 1*H*-indazole (**B-11**) could act simultaneously as H-bond donor and H-bond acceptor and double H-bonds (one N···H–O bond and one O–H···N bond) are formed. However, all the other complexes could only form a single H-bond thus weaker than the complex of 1*H*-indazole (**B-11**) and **C4PA**. When the **C4PA** forms a H-bond with a secondary amine group in the heterocyclic ring, the amine group donates its proton to **C4PA** instead of accepting a proton from **C4PA** (O–H···N bond) as the amine nitrogen atom has a planar sp² hybrid and its lone

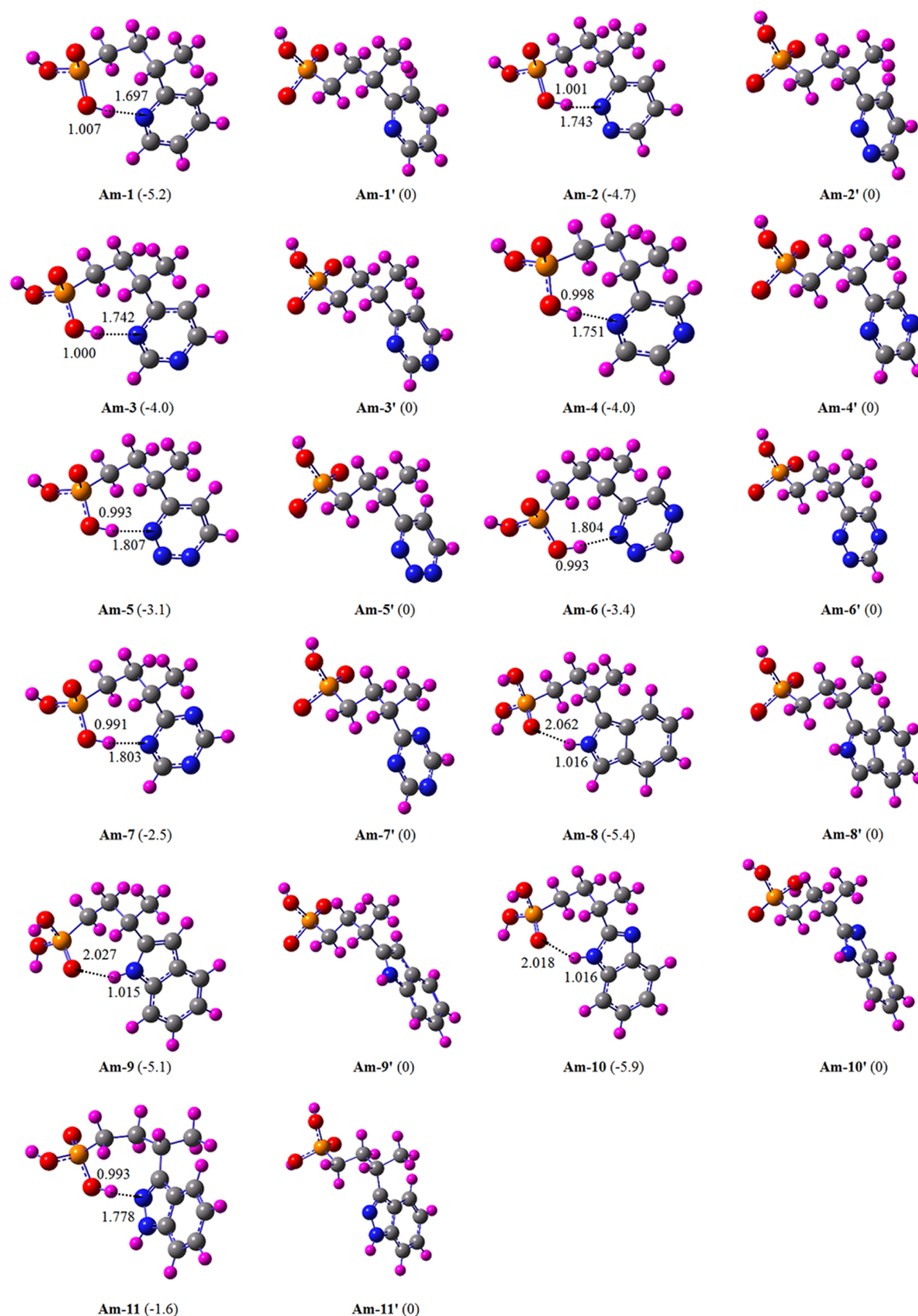


Figure 2. Intramolecular H-bond and bonding energies (numbers in parentheses, units: kcal·mol⁻¹) in the acid–base amphoteric molecules evaluated at the B3LYP/6-311+G(2d,p)//MP2/6-311+G(2d,p) level of theory.

pair is part of the aromatic system. On the other hand, if **C4PA** forms a H-bond with a planar sp² nitrogen atom without a hydrogen atom bonded (the imine nitrogen atom), the **C4PA**

acts as H-bond donor and the imine nitrogen atom as H-bond acceptor, forming a N···H–O bond. The H-bond distance of O···H in complexes of **C4PA** and indole (**B-8**) and of **C4PA**

and 2*H*-isoindole (**B-9**) are at 1.991 and 1.965 Å, much longer than the H-bond distance of N⋯H at about 1.74 Å. The H-bond angles also show the same tendency, as the O–H⋯N bond usually has an angle at about 150°, while the N⋯H–O bond has an angle at about 175°. Besides the H-bond, the structures of acid–base complexes are also influenced by the weak O⋯H–C interaction, where the carbon atom is directly bonded to an imine nitrogen atom, with an O⋯H distance at about 2.199–2.384 Å. Therefore, it could be concluded that the structures of acid–base complexes are determined by three types of interactions, the N⋯H–O bond, O–H⋯N bond, and O⋯H–C interaction, the N⋯H–O bond is stronger than the O–H⋯N bond, and O⋯H–C interaction is the weakest.

These results are consistent with the acid–base complexes of **C4PA** and heterocycles of 5-membered ring, where the complex of **C4PA** and pyrazole forms one O–H⋯N bond and one N⋯H–O bond, the complex of **C4PA** and imidazole forms a strong N⋯H–O bond, and the complex of **C4PA** and pyrrole forms a weak O–H⋯N bond.¹⁸

3.3. Intramolecular H-Bond. The optimized structures and parameters of acid–base amphoteric molecules were summarized in Figure 2 and Table 3. The H-bond structures

Table 3. Intramolecular H-Bond Parameters for Acid–Base Amphoteric Molecules

system	$d_{\text{N-H}}$ (Å)	$d_{\text{O-H}}$ (Å)	$\angle \text{N(C)HO}$ (deg)	ν (cm^{-1})	$\Delta E_{\text{HB}}^{\text{inter}}$ (kcal mol^{-1})
Am-1	1.697	1.007	173.3	2957	−5.2
Am-2	1.743	1.001	170.7	3083	−4.7
Am-3	1.742	1.000	171.8	3106	−4.0
Am-4	1.751	0.998	171.3	3133	−4.0
Am-5	1.807	0.993	168.3	3357	−3.1
Am-6	1.804	0.993	168.0	3249	−3.4
Am-7	1.803	0.991	163.7	3271	−2.5
Am-8	1.016	2.062	146.4	3512	−5.4
Am-9	1.015	2.027	151.2	3518	−5.1
Am-10	1.016	2.018	148.1	3502	−5.9
Am-11	1.778	0.993	173.7	3236	−1.6

are similar to the acid–base complexes despite the configurational restriction of intramolecular H-bond. For the N⋯H–O bond, the N⋯H bond distances are at about 1.766 Å, while, for the O–H⋯N bond, the average O⋯H bond distance is about 2.036 Å, much longer than the N⋯H bond distance. The H-bond angles also show a similar tendency as that in the acid–base complexes, with an average N⋯H–O bond angle of 170.1° and O–H⋯N bond angle of 148.6°. However, the intramolecular H-bond energies are much lower than that of an intermolecular H-bond and vary differently from the H-bond structures. For the O–H⋯N bond, the average bonding energy is −5.5 kcal mol^{-1} , and it is stronger than the N⋯H–O bonding at about −3.6 kcal mol^{-1} . In addition, double H-bond is impossible for the intramolecular H-bond because of configurational restriction despite the possibility if only the chemistry nature of H-bond acceptor and H-bond donor is considered.

3.4. ^1H NMR and ^{31}P NMR Chemical Shifts and Proton Exchange between Acid and Base. ^1H NMR chemical shift reflects the chemical environment of a proton, since a tightly bound proton is shielded and a loosely bound proton is deshielded by electron cloud. The ^1H NMR of **C4PA** and eight of the heterocycles and their complexes are shown in Figure 3,

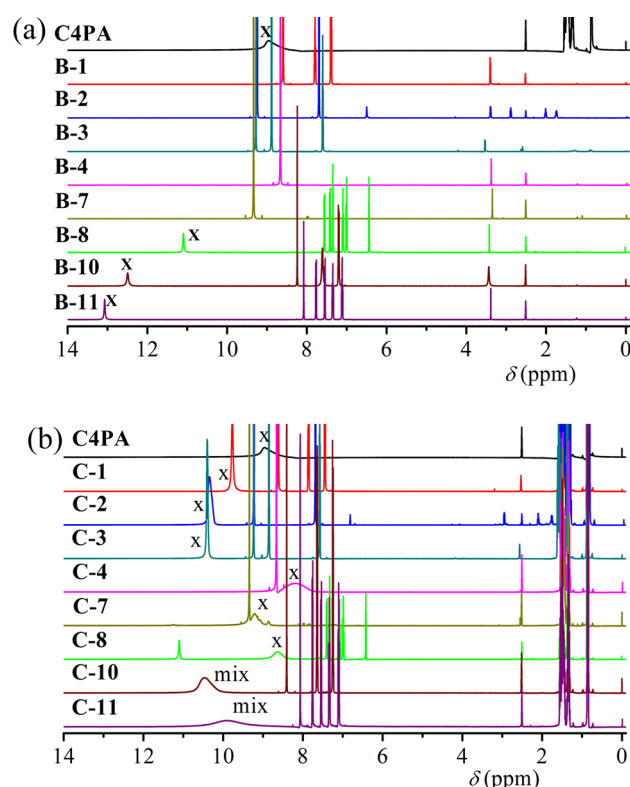


Figure 3. ^1H NMR of (a) butanephosphonic acid and heterocycles and (b) their complexes.

and the peak assignments are summarized in Figure 4. Since only the acidic protons are transportable, we are going to discuss the ^1H NMR signals or the chemical shifts of the acidic protons in this work.

The acidic protons are usually significantly deshielded with chemical shifts at 8 ppm or even greater, and the chemical shift of acidic protons of **C4PA** is 8.928 ppm in $\text{DMSO-}d_6$ (Table 4). If a heterocyclic base is added and a H-bond is formed between the **C4PA** and the heterocyclic base, the acidic proton will be further deshielded. Therefore, the H-bond and proton exchange between a **C4PA** and a heterocyclic base could be studied by comparison of the ^1H NMR chemical shift of **C4PA**, heterocyclic base, and their complex.

Besides the acidic proton of **C4PA**, the heterocyclic bases 1*H*-benzimidazole (**B-10**), 1*H*-indazole (**B-11**), and indole (**B-8**) also possess an acidic proton (N–H) with chemical shifts at 12.493, 13.070, and 11.094 ppm. When 1*H*-benzimidazole (**B-10**) or 1*H*-indazole (**B-11**) is added to **C4PA** forming an acid–base complex (**C-10** or **C-11**), the two peaks from **C4PA** and heterocyclic base are mixed into a single peak, indicating the fast proton exchange between **C4PA** and heterocyclic base. However, if indole (**B-8**) is added to **C4PA** forming an acid–base complex (**C-8**), the two peaks from **C4PA** and indole (**B-8**) do not mix into a single peak, indicating no proton exchange or slow proton exchange than the measurement of ^1H NMR at the time scale of milliseconds. This characteristic is consistent with the fact that indole (**B-8**), unlike most amines, is an acid with a pK_a of 16.2 (for the N–H proton), and very strong acids such as hydrochloric acid are required to protonate indole (**B-8**) (the protonated form has a pK_a of −3.6).⁴⁸ These characteristics are also consistent with the calculated H-bond energies of the acid–base complexes, the H-bond energies for complexes of **C4PA** and 1*H*-benzimidazole (**B-10**), or 1*H*-

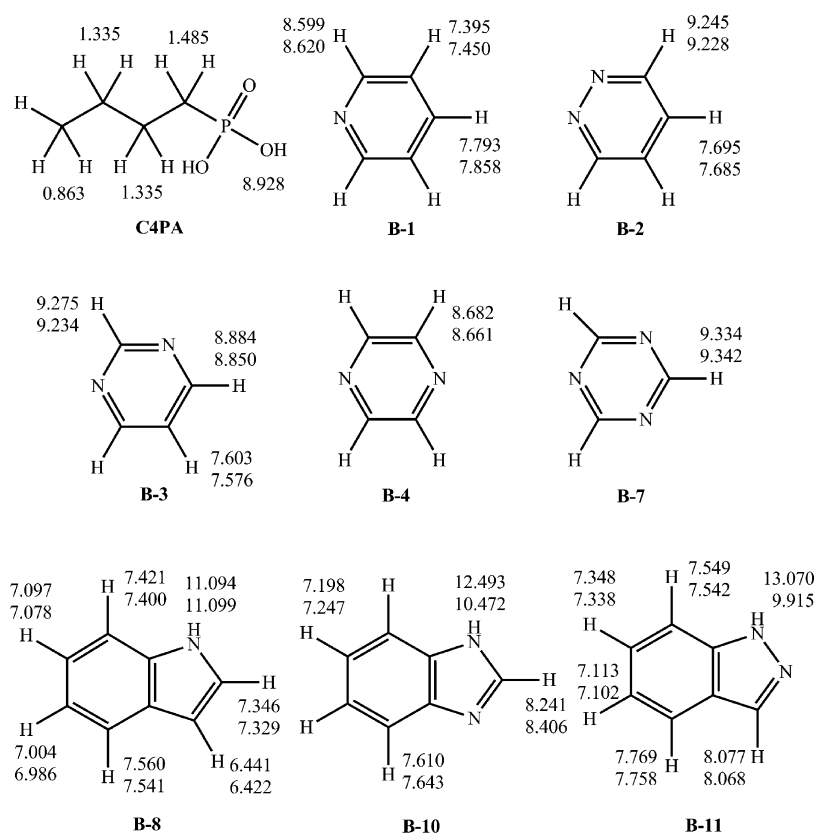


Figure 4. ^1H NMR chemical shifts (peak assignment) of the **C4PA**, heterocycles (upper number), and their complexes (lower number) in $\text{DMSO}-d_6$.

Table 4. ^1H NMR and ^{31}P NMR Chemical Shifts (Units: ppm)

	^1H NMR ^a	^1H NMR ^b	^{31}P NMR ^c
C4PA	8.928		29.875
C-1		9.770	29.066
C-2		10.342	29.345
C-3		10.398	29.623
C-4		8.185	29.484
C-7		9.210, 8.863	29.419
C-8	11.094	11.099, 8.630	29.487
C-10	12.493	10.472	28.002
C-11	13.070	9.915	29.481

^a ^1H NMR chemical shifts of the acidic proton of isolated **C4PA** or heterocyclic bases. ^b ^1H NMR chemical shifts of the acidic proton of the complexes of **C4PA** and heterocyclic bases. ^c ^{31}P NMR chemical shifts of **C4PA** and complexes of **C4PA** and heterocyclic bases.

indazole (**B-11**), or indole (**B-8**) are -14.0 , -17.7 , and -9.8 kcal mol^{-1} , respectively. Therefore, it is concluded that strong H-bond interaction could cause fast proton exchange.

For the complex of **C4PA** and heterocyclic base without acidic proton, we compared the chemical shift between **C4PA** and its complex with heterocyclic base. For the complex of **C4PA** and pyridine (**B-1**), the chemical shift of the acidic proton is shifted downfield 0.842 ppm from 8.928 to 9.770 ppm, and the H-bond energy of the complex (**C-10**) is -12.3 kcal mol^{-1} . For the complex of **C4PA** and pyridazine (**B-2**) or pyrimidine (**B-3**), the chemical shift is also shifted downfield 1.414 or 1.470 ppm, and the corresponding H-bond energy is -12.6 or -10.1 kcal mol^{-1} , respectively. Different characteristics were observed for the complex of **C4PA** and pyrazine (**B-**

4) or 1,3,5-triazine (**B-7**): the ^1H NMR chemical shift of the complex of **C4PA** and pyrazine (**B-4**) is shifted upfield 0.753 ppm, and that of **C4PA** and 1,3,5-triazine (**B-7**) splits into two peaks, one downfield 0.282 ppm and the other upfield 0.065 ppm, indicating the existence of protons in different chemical environments and thus complicated H-bond characteristics.

In the ^1H NMR of bases (Figure 3a), water peaks are clearly shown because of residual water molecules existing in the hydrophilic bases. On the other hand, the ^1H NMR of **C4PA**, which is also hydrophilicity, and the acid–base complexes do not show any water peaks as the residual water molecules are bound by the phosphonic acid groups and no free water molecules exist in the testing solutions. Though residual water molecules have a very strong effect on the H-bond characteristics and the proton conductivity and should be avoided in the ^1H NMR experiments, residual water cannot be avoided in any operational PEMFCs.

The chemical shift for ^{31}P NMR reflects the chemical environment of the phosphonic acid group, and the H-bond characteristics of the phosphonic acid group in the acid–base complex could be studied by comparison of ^{31}P chemical shifts between an isolated **C4PA** or its complex with a heterocyclic base. The ^{31}P NMR chemical shift for **C4PA** is 29.875 ppm, and significant upfield shift was observed in the acid–base complexes. When 1*H*-benzimidazole (**B-10**), a medium strength base, is added to **C4PA** solution in $\text{DMSO}-d_6$, the ^{31}P chemical shift is shifted upfield 1.873 ppm owing to the attraction of acidic proton of **C4PA** by 1*H*-benzimidazole (**B-10**), and the leftover electron cloud on the phosphonic acid group that shields the ^{31}P atom. The other heterocyclic bases, such as pyridine (**B-1**), will also attract proton from **C4PA** and

leave the electron cloud over the phosphonic acid group as indicated by the upfield shift of the chemical shift for ^{31}P NMR. These characteristics are consistent with the density functional theory calculations in terms of H-bond structures and H-bond energies.

3.5. Temperature Dependent ^1H NMR Spectra. In order to study the proton exchange reaction between the **C4PA** and heterocycles, temperature dependent ^1H NMR experiments were carried out using $\text{THF-}d_8$ as solvent for complexes **C-8**, **C-10**, and **C-11**. The ^1H NMR experiments were conducted in the temperature range between 20 and 100 $^\circ\text{C}$ for **C-8** (Figure 5a) and between -100 and 20 $^\circ\text{C}$ for **C-11** (Figure 5b). However, the temperature dependent ^1H NMR experiments failed for **C-10** because **C-10** begins to precipitate at 0 $^\circ\text{C}$.

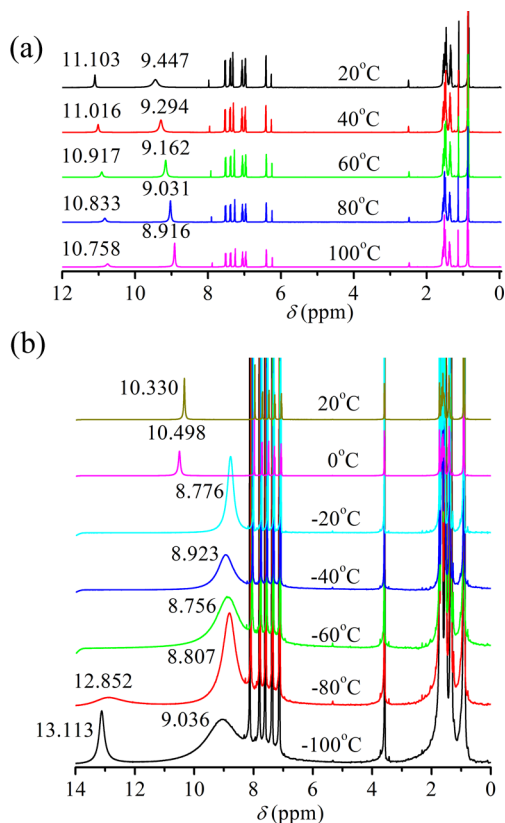


Figure 5. Temperature dependence of ^1H NMR spectra of (a) **C-8** and (b) **C-11**.

Since we are interested in the proton transport characteristics, only the peaks that correspond to the active protons will be discussed in this context. For **C-8**, the peaks for active protons undergo systematic changes as the temperature is increased from 20 to 100 $^\circ\text{C}$ in peak positions and widths. As expected, the peak for **C4PA** (centered at about 9 ppm) gradually shifts from low field at 9.447 ppm to high field at 8.916 ppm and narrows continuously as the temperature is increased. On the other hand, the peak for **B-8** (centered at about 11 ppm) also gradually shifts from low field to high field but continuously widens. In addition, these two peaks never mix into a single peak. Therefore, it was concluded that **C-8** does not undergo proton exchange up to 100 $^\circ\text{C}$, consistent with the fact that **B-8** is actually an acid and cannot be deprotonated by the medium strength acid **C4PA**.⁴⁸ For **C-11**,

the peaks for active protons undergo great changes in the temperature range of ^1H NMR experiments. On the one hand, these two peaks do not mix into a single peak because the proton exchange is hindered below -70 $^\circ\text{C}$; on the other hand, only one mixed peak is observed attributing to the fast proton exchange above -70 $^\circ\text{C}$. In addition, the peak position and width also undergo great changes at about -10 $^\circ\text{C}$: the peak is narrow and centered at about 10.4 ppm above -10 $^\circ\text{C}$; however, the peak shifts high field to about 8.8 ppm, and greatly widens below -10 $^\circ\text{C}$. From these characteristics, it was concluded that the proton exchange is hindered below about -70 $^\circ\text{C}$.

4. CONCLUSIONS

From the density functional theory calculations, it is concluded that a H-bond is formed between **C4PA** and heterocycles with the phosphonic acid group as both H-bond donor and H-bond acceptor, and imine nitrogen atom as H-bond acceptor and amine group as H-bond donor. For the complex of **C4PA** and heterocycles with both imine nitrogen atom and amine, double H-bonds are possible if configuration is allowed. Therefore, the strongest H-bond interaction is observed in the complex of **C4PA** and 1*H*-indazole (**B-11**) because of double H-bonds. For the complex with a single H-bond, the strongest H-bond is observed in the complex of **C4PA** and 1*H*-benzimidazole (**B-10**). The H-bond between **C4PA** and amine is weaker than that between **C4PA** and imine nitrogen atom in terms of structural and energetic parameters. The intramolecular H-bond is weaker than the intermolecular H-bond because of configurational restriction.

From the ^1H NMR chemical shifts, fast proton exchange is observed between **C4PA** and 1*H*-benzimidazole (**B-10**) or 1*H*-indazole (**B-11**); however, it is not observed between **C4PA** and indole (**B-8**). For the complexes of **C4PA** and heterocycles, significant downfield shifting for ^1H NMR chemical shift is observed, indicating the loosening of acidic protons and thus facilitating proton transport. In addition, upfield shifting for ^{31}P NMR chemical shift is observed, indicating the attraction of proton from a phosphonic acid group by a heterocyclic group. From the density functional theory calculations and ^1H NMR and ^{31}P NMR spectroscopy, it could be concluded that the nitrogenous heterocycles containing both proton donor (amine) and acceptor (imine) facilitate the proton transport, and it is proposed that polymeric material tethered with a 1*H*-indazole (**B-11**) and benzimidazole (**B-10**) ring is favorable for HT-PEM.

Moreover, density functional theory calculations and ^1H NMR spectroscopy could be applied to the design of proton conducting material by screening out plausible acidic and basic functional groups that facilitate proton transport under dehydrated or even anhydrous states.

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Notes

The authors declare no competing financial interest.

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