CHAPTER V

SYNTHESIS AND STRUCTURAL CHARACTERIZATIONS OF AMINOTRIS[2-(BENZIMIDAZOL-2-YL)ETHYL]METHANE: MULTI-BENZIMIDAZOLE MOIETY AS PROTON CONDUCTIVE SPECIES IN ANHYDROUS POLYMER ELECTROLYTE MEMBRANE

5.1 Abstract

A trifunctional benzimidazole derivative, i.e., aminotris[2-(benzimidazol-2-yl)ethyl]methane, is designed and synthesized. By simply modified nitromethanetripropionic acid to acid chloride followed by the reaction with phenylenediamine, an intermediate tris[2-(benzimidazol-2-yl)ethyl]nitromethane is obtained. The reduction using Pd/C catalyst successfully leads to aminotris[2-(benzimidazol-2-yl)ethyl]methane. The present work shows the preparation of tri-benzimidazole molecule with amino group which is useful for further modification with polymer to obtain a novel type of anhydrous polymer electrolyte membrane (PEM).

Keywords: Benzimidazole, Proton conductive molecule, Polymer electrolyte membrane

5.2 Introduction

The most currently used polymer electrolyte membranes (PEM) in polymer electrolyte membrane fuel cell (PEMFC) are based on perfluorosulfonic acid polymers such as Nafion® due to its excellent proton conductivity (~0.1 S/cm at 80 °C under fully hydrated condition) with good chemical stability.[1-3] Proton conductive property of the hydrous-based membrane is generated by proton movement through the hydrogen bond network of water clusters.[4] Consequently, the decreasing of water content in the membrane results in lowering of proton conductivity at high temperature.[3]

Since high temperature PEMFCs are required for accelerating proton movement and reducing carbon monoxide poisoning on catalyst surface, heterocycles have been extensively developed to become a promising proton conductive molecule for using in anhydrous PEM for the past decades. The amphoteric character of heterocycles plays an important role in proton transferring through forming and breaking of hydrogen bonds.[5] A number of polymers based on N-containing heterocycles such as poly(4-vinylimidazole)[6], polybenzimidazole[7], poly(1,2,4-vinyltriazole)[8], and polyimide[9] have been investigated as potential polymers for PEM. It should be noted that in practical, an additional acid treatment of those heterocyclic based polymers is still required..

In our previous work, the systematic study on benzimidazole derivatives with different number of benzimidazole groups clarified to us that among mono-, di-, and trifunctional benzimidazole derivatives, the trifunctional one shows the most significant proton conductivity. The single crystal analysis declares the helical H-bond network of the trifunctional benzimidazole derivative which might be the main factor in enhancing the proton transfer resulting in the significant proton conductivity.

It comes to our question about how to develop polymer chains with trifunctional benzimidazole. In order to answer this question, a molecule which not only contains the trifunctional groups of benzimidazole but also the reactive species for the conjugation with polymer chains is needed. Based on this viewpoint, the present work, thus, proposes the molecular design and synthesis of their packing structure. However, in order to apply those derivatives, the conjugation with polymer backbone is needed. , On this viewpoint, the present work focuses on the molecular design and synthesis of aminotris[2-(benzimidazol-2-yl)ethyl]methane. The conjugation of this compound onto polymer chains to obtain a unique PEM with trifunctional benzimidazole groups is in progress.

5.3 Experimental

5.3.1 Materials

Nitromethanetripropionic acid, 1,2-phenylenediamine, Pd/C (10% palladium on activated carbon), and deuterated dimethyl sulfoxide (DMSO-*d*6) were obtained from Aldrich Co. Thionyl chloride ($SOCl_2$), Ammonia solution, and *p*-xylene were purchased from Wako Co. Sodium carbonate anhydrous was obtained from Fluka Co. Methanol and acetic acid were received from Labscan Co. All chemical were used as received.

5.3.2 Synthesis of Tris[2-(benzimidazol-2-yl)ethyl]nitromethane, 2

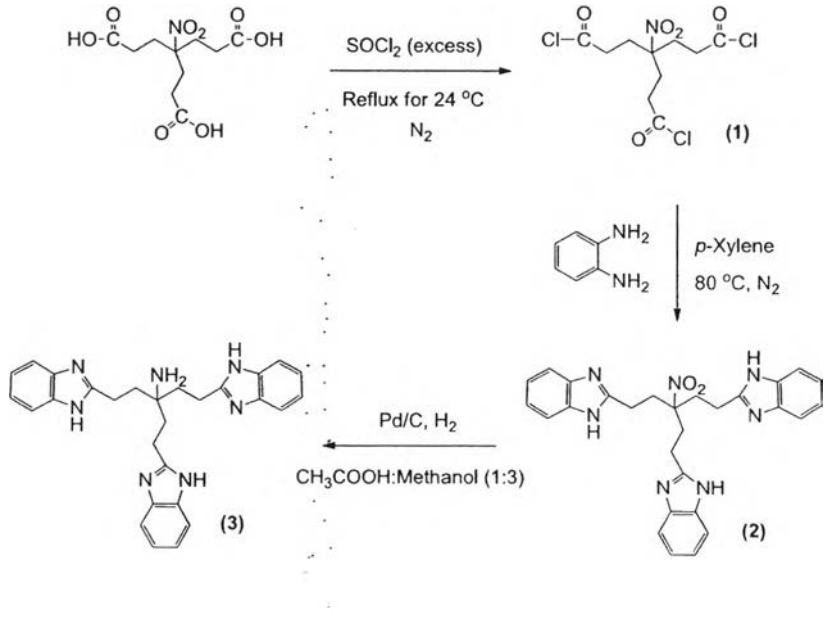
Nitromethanetripropionic acid (2.0 g, 7.21 mmol) was refluxed in $SOCl_2$ solution (30 ml) under N_2 atmosphere for 24 h. (Scheme 5.1). The excess $SOCl_2$ was removed under vacuum to obtain brown viscous of 4-(3-chloro-3-oxopropyl)-4-nitroheptanedioyl dichloride, **(1)**. The product **1** was then dissolved in *p*-xylene (150 ml) before slowly dropwising in *p*-xylene (50 ml) containing 1,2-phenylenediamine (4.67 g, 43.2 mmol). The mixture was vigorously stirred at 80 °C under nitrogen for 24 h. The yellow precipitates obtained were collected. The excess reagent was removed by washing the precipitates with xylene. The crude products were further suspended in hot water and subsequently washed with ammonia solution at 0 °C. The light brown precipitates were collected and washed with cool water for several times and dried in vacuum to obtain **2**.

4-(3-chloro-3-oxopropyl)-4-nitroheptanedioyl dichloride, 1. FTIR (KBr, ν cm^{-1}) 2948 and 2882 (m, C-H stretching), 1795 (s, C=O stretching), 1544 (vs, NO_2 stretching), 1450 (m, CH_2 deformation), 968 (m, C-C stretching), 609 (s, NO_2 bending) and 445 (s, Cl-C=O in plane deformation).

Tris[2-(benzimidazol-2-yl)ethyl]nitromethane, 2. Yield 70.3% FTIR (KBr, ν cm^{-1}) 3600-2400 (br, hydrogen bonded N-H stretching), 1623(w, C=N stretching), 1538 (vs, NO_2 stretching), 1452 (s, C=C stretching), 1272 (s, C-N stretching), and 744 cm^{-1} (s, C-H bending of aromatic ring). ^1H NMR (δ ppm, 500 MHz, DMSO-d_6, 298 K): 9.41 (3H, s, N*H*), 7.52-7.47 (6H, m, Ar*H*), 7.16-7.12 (6H,

m, Ar*H*), 2.97-2.82 (6H, m, CH_2), 2.69-2.60 (6H, m, CH_2). ESI-MS calcd for $C_{28}H_{28}N_7O_2$ *m/z* 494.57, found 494.2306 $(M+H)^+$.

Scheme 5.1 Synthesis of **1**, **2** and **3**



5.3.3 Synthesis of Aminotris[2-(benzimidazol-2-yl)ethyl]methane, 3

A mixture of **2** (0.3 g, 0.61 mmol) and Pd/C (0.5 g) in acetic acid-methanol (1:3 v/v, 12 ml) were purged with H_2 under stirring at room temperature for 24 h. The catalyst was removed by filtration. The filtrate was evaporated under vacuum. The crude product was treated with 0.5 M Na_2CO_3 (100 ml), washed with cold water for several times, and dried under vacuum to provide brown solid of **3**.

Aminotris[2-(benzimidazol-2-yl)ethyl]methane (3) Yield 91.2 % FTIR (KBr, ν cm^{-1}) 3600-2400 (br, hydrogen bonded N-H stretching), 1621 (w, C=N stretching), 1575 (s, NH_2 deformation), 1453 (s, C=C stretching), 1271 (s, C-N stretching), and 742 cm^{-1} (s, C-H bending of aromatic ring). ^{1}H NMR (δ ppm, 500 MHz, DMSO-d_6, 298 K): 12.24 (3H, s, N*H*), 7.53-7.41 (6H, m, Ar*H*), 7.12-7.11 (6H, m, Ar*H*), 2.97-2.94 (6H, m, CH_2), 1.97-1.93 (6H, m, CH_2). ESI-MS calcd for $C_{28}H_{30}N_7$ *m/z* 464.58, found 464.5584 $(M+H)^+$.

5.3.4 Characterization

Fourier transform infrared (FTIR) spectra were collected on a Thermo Nicolet Nexus 670 with 32 scans at a resolution of 2 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed by using deuterated triglycerinesulfate detector (DTGS).

^{1}H nuclear magnetic resonance (NMR) spectra were recorded in DMSO-*d*6 on a BrukerAvance 500 MHz NMR spectrometer at room temperature.

Electrospray ionization mass spectra (ESI-MS) were analyzed by using a MicroTOF II, Bruker instrument equipped with Bruker Compass DataAnalysis 4.0 software with positive ion polarity mode. The capillary voltage was set at 4500 V.

5.4 Results and Discussion

5.4.1 Synthesis of 2

To carry out the amidation reaction of diamines with high reactive functional group of acid chlorides, carboxylic acid groups of nitromethanetripropionic acid were activated by $SOCl_2$ to obtain acid chloride derivative of **1**. The reaction was traced by FTIR spectra. Initially, the reaction between nitromethanetripropionic acid and $SOCl_2$ was done at room temperature for at least 3 days however only some carboxyl groups were converted into acid chlorides as observed from the appearing of a new peak at 1795 cm^{-1} belonging to C=O stretching mode of acid chloride and the remaining of the peak at 1716 cm^{-1} belonging to C=O stretching mode of carboxylic acid (Figure 5.1b). Thus, the reaction was performed at reflux temperature under nitrogen. After one day, a complete disappearance of the peaks at 1716 cm^{-1} and at 3400-2400 cm^{-1} (H-bonded OH stretching) as well as the appearance of the strong absorption intensity at 1795 cm^{-1} confirms the formation of **1** as shown in Figure 5.1c.

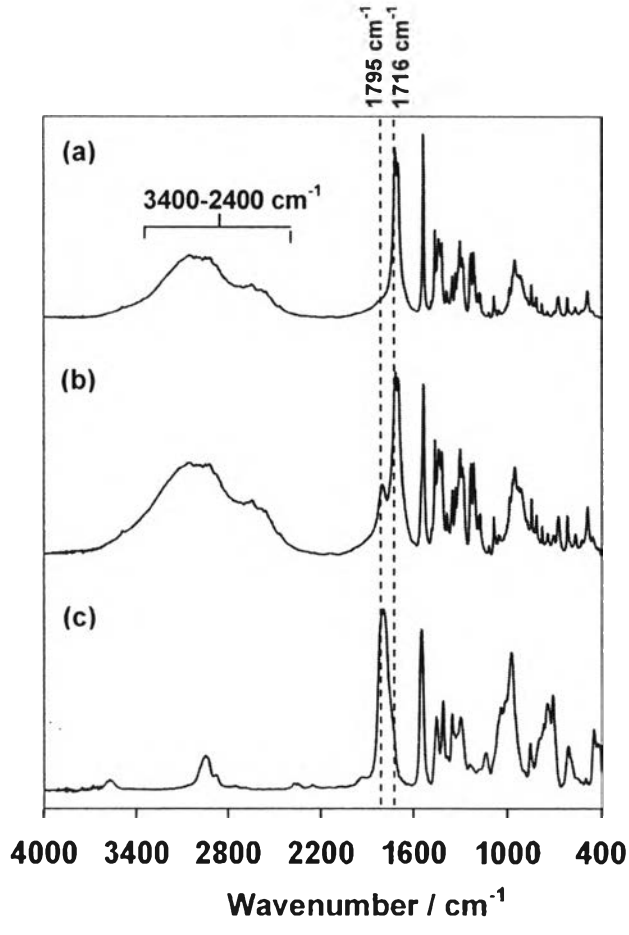


Figure 5.1 FTIR spectra of (a) nitromethanetripropionic acid, and the reaction between nitromethanetripropionic acid and $SOCl_2$ at (b) room temperature for 3 days, and (c) reflux temperature for a day.

Since **1** is very active, after removing excess $SOCl_2$ from the reaction (step 1, scheme 5.1), it was immediately dissolved in *p*-xylene. Benzimidazole derivative, **2**, was prepared by dropwising the solution of **1** into a vigorously stirred solution of an excess amount of *1,2*-phenylenediamine. The reaction was done at 80 °C under N_2 atmosphere for one day. The product was collected and purified accordingly by xylene, ammonia solution, and cool water. The characteristic FTIR spectrum of **2** is shown in Figure 5.2. The formation of benzimidazole structure is observed at 3600-2400 cm^{-1} (hydrogen bonded N-H stretching), 1623 cm^{-1} (C=N stretching), 1455 cm^{-1} (C=C stretching), 1272 cm^{-1} (C-N stretching), and 743 cm^{-1} (C-H bending of

aromatic ring). Another characteristic peak of **2** is at 1538 cm^{-1} belonging to NO_2 stretching.

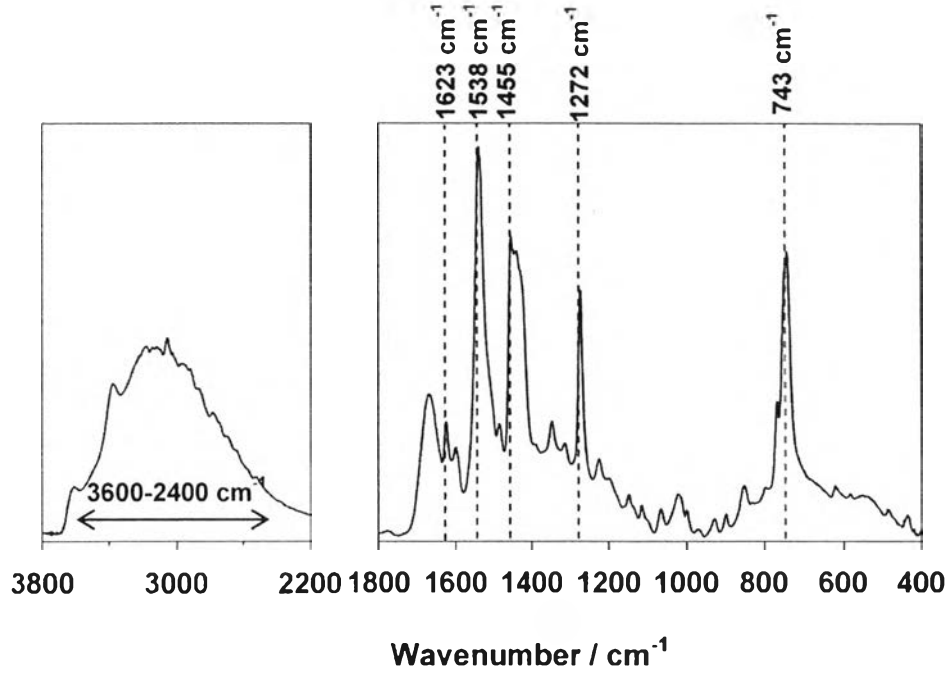


Figure 5.2 FTIR spectrum of **2**.

^{1}H NMR spectrum of **2** is shown in Figure 5.3. The chemical shifts at 7.52-7.47 and 7.16-7.12 ppm are assigned to protons in benzene ring and at 2.97-2.82 and 2.69-2.60 ppm are assigned to methylene protons. The peak at 9.41 ppm indicates the presence of the NH of benzimidazoles. ESI-MS spectrum confirms the structure of **2** as observed the parent peak $(M+H)^+$ at *m/z* = 494.5218 (molecular weight of **2** is 494.57) (Figure 5.4).

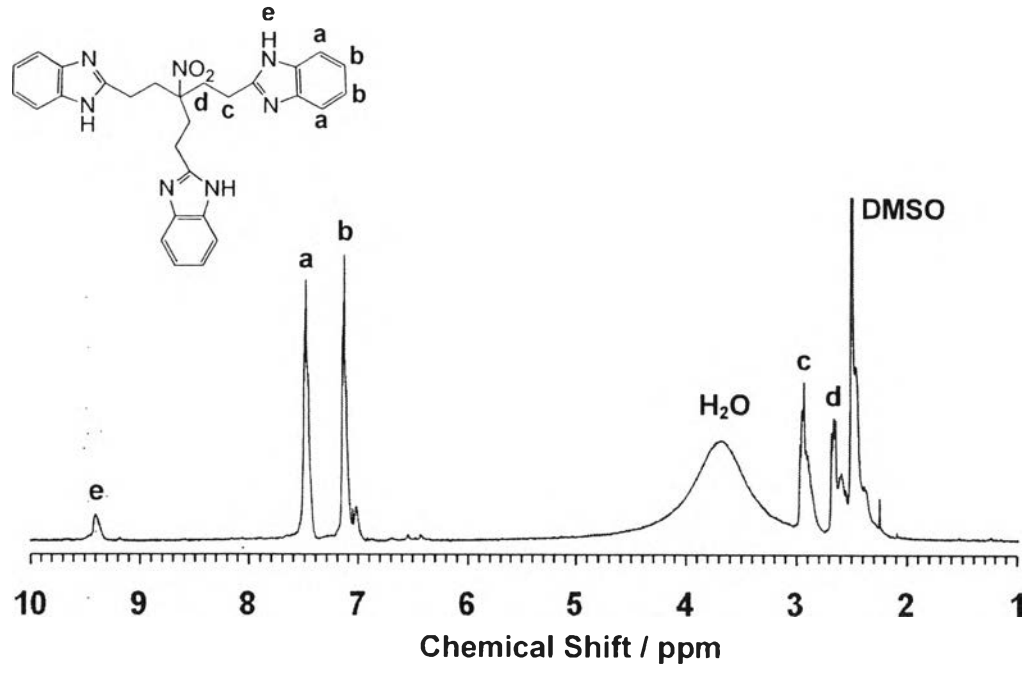


Figure 5.3 ^{1}H NMR spectrum of **2**.

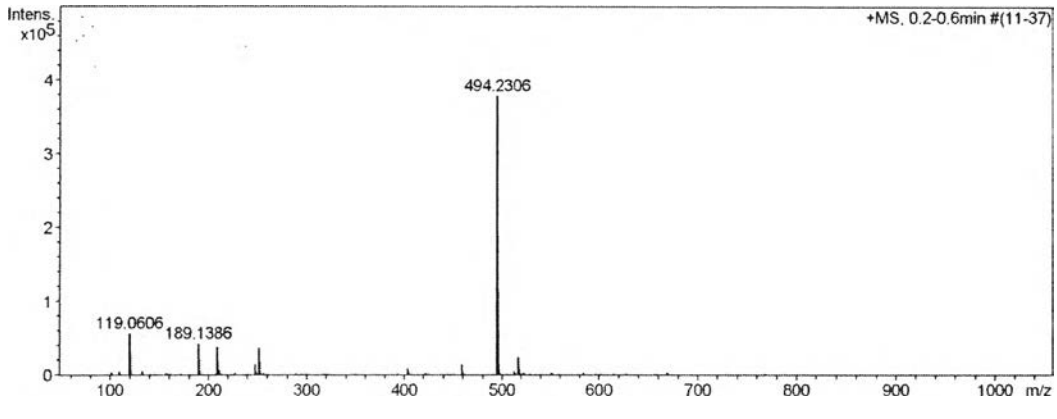


Figure 5.4 ESI-MS spectrum of **2**.

5.4.1 Synthesis of 3

With an aim to functionalize multifunctional benzimidazoles on a polymer chain to form PEM, the nitro groups (NO_2) of **2** has to be converted into amino groups (NH_2). Firstly, the reduction of the nitro groups was done in methanol at

room temperature similar to the case of the reduction of bis-3-nitro-4-[3-(triethylammoniumsulfonato)phenylamino]-phenyl sulfone using Pd/C as a catalyst as reported by Jouanneau et al. [10] However, the reaction was not successful. The transformation of **2** to **3** was successfully performed in acetic acid-methanol (1:3 v/v) by using Pd/C as a catalyst. The method was adapted from the reduction of tris[2-(1-methylbenzimidazol-2-yl)ethyl]nitromethane by Pd/C in acetic acid-water (1:3 v/v) reported by Casella et al.[11] As compared to FTIR spectrum of **2,** the disappearance of the peak at 1538 cm^{-1} (NO_2 stretching) in addition to the appearance of the peak at 1539 cm^{-1} (NH_2 deformation) indicates the successful reduction (Figure 5.5). The characteristic absorption bands of benzimidazole are at 3600-2400 cm^{-1} (hydrogen bonded N-H stretching), 1623 cm^{-1} (C=N stretching), 1454 cm^{-1} (C=C stretching), 1272 cm^{-1} (C-N stretching), and 744 cm^{-1} (C-H bending of aromatic ring).

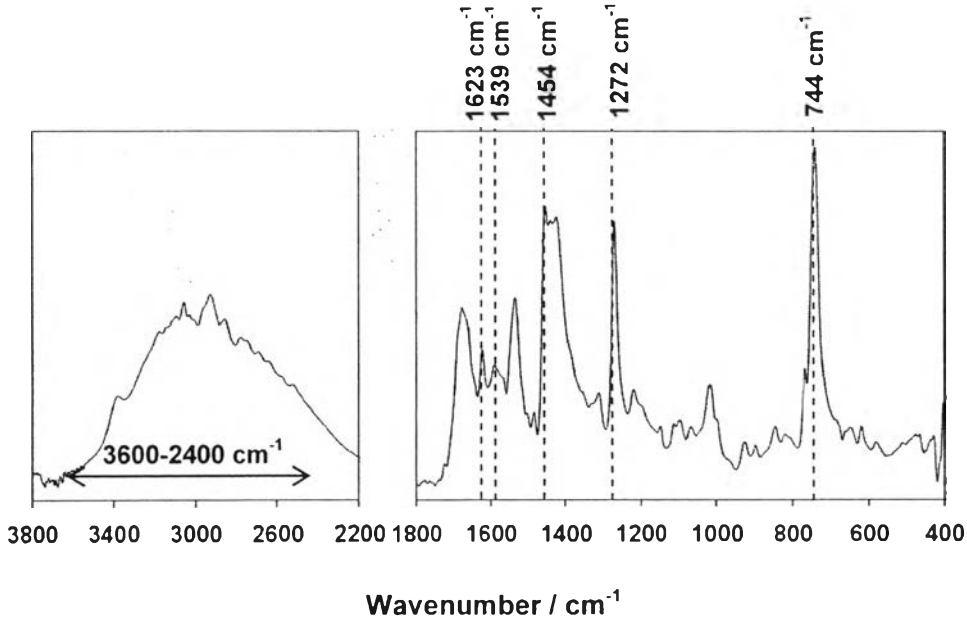


Figure 5.5 FTIR spectrum of **3**.

^{1}H NMR spectrum (Figure 5.6) shows the chemical shifts of **3** at 12.24 ppm (N-H protons), 7.53-7.41 and 7.12-7.11 ppm (protons of the benzene ring), and 2.97-2.94 and 1.97-1.93 ppm (methylene protons). In addition, ESI-MS spectrum confirms

the successful preparation of **3** from a parent peak $(M+H)^+$ at m/z = 464.5584 (molecular weight of **3** is 463.58) as shown in Figure 5.7.

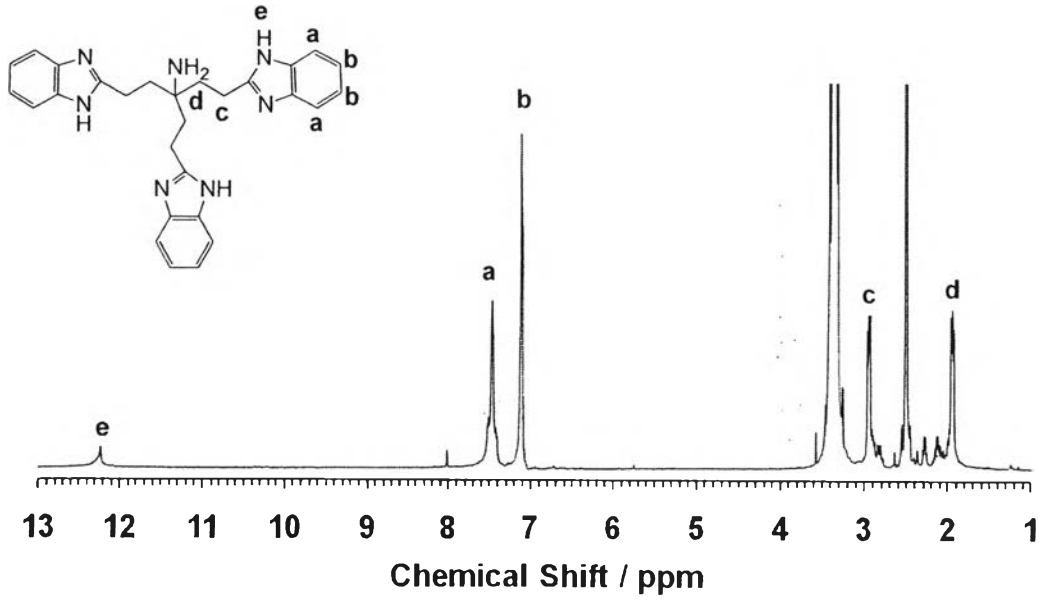


Figure 5.6 ^{1}H NMR spectrum of **3**.

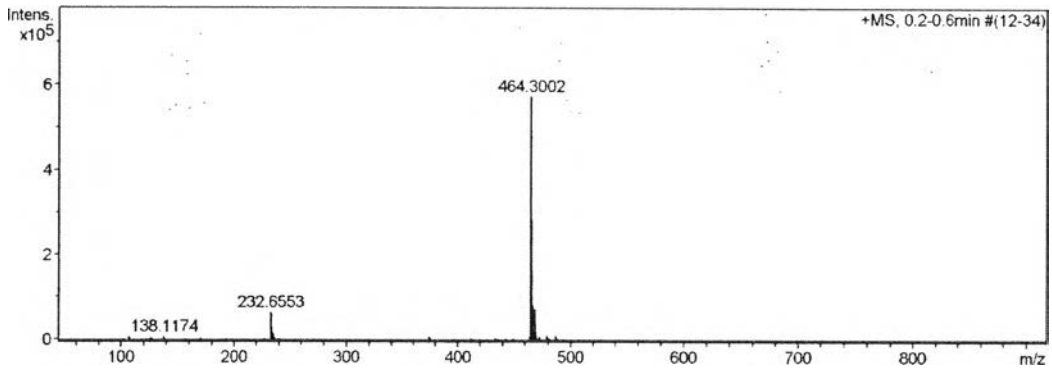


Figure 5.7 ESI-MS spectrum of **3**.

Here, multi-benzimidazole compound of **3** was successfully prepared as detailed analysed by the spectroscopy techniques. The work will extend to functionalization of the multi-benzimidazole compound onto polymer chain to obtain polymer electrolyte containing multi-benzimidazole moiety. In our viewpoint, poly(acrylic acid) is appropriate for this study because its acidic property can act as proton donor while multi-benzimidazole structure is expected to offer the cluster of

hydrogen bond network for proton hopping. Based on the concept of proton donor-acceptor of acid and base structures, multi-benzimidazole functionalized poly(acrylic acid) will be developed for the use as PEM under water free condition.

5.5 Conclusions

The work succeeded in preparing of aminotris[2-(benzimidazol-2-yl)ethyl]methane with multi-benzimidazole moiety as proton conductive species and amine group for further modification. To enhance proton conductivity of the heterocycle species in a polymer electrolyte membrane with proton donating properties of an acidic polymer, the functionalization of aminotris[2-(benzimidazol-2-yl)ethyl]methane onto acid polymer of poly(acrylic acid) is under investigation. In addition, the studies on the effects of acid-base content on the proton conductivity as well as the effects of temperature on hydrogen bonding, molecular packing structure and chain mobility related to proton conduct will be clarified.

5.6 Acknowledgements

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5.7 References

1. Ahmad, H.; Kamarudin, S.K.; Hasran, U.A.; Daud, W.R.W. Int. J. Hyd. Energy **2010**, 1-16.
2. Mauritz, K.A.; Moore, R.B. Chem. Rev. **2004**, 104, 4535-4585.

3. Hickner, M.A.; Ghassemi, H.; Kim, Y.S.; Einsla, B.R.; McGrath, J.E. Chem. Rev. **2004**, 104, 4587-4612.
4. Agmon, N. Chem. Phys. Lett. **1995**, 244, 456-462.
5. Münch, M.; Kreuer, K. D.; Silvestri, W.; Maier, J.; Seifert, G. Solid State Ionics **2001**, 145, 437-443.
6. Bozkurt, A.; Meyer, W.H. Solid State Ionics **2001**, 138, 259–265.
7. Jiang, F.; Pu, H.; Meyer, W.H.; Guan, Y.; Wan, D. Electrochim. Acta **2008**, 53, 4495–4499.
8. Pu, H.; Ye, S.; Wan, D. Electrochim. Acta **2007**, 52, 5879–5883.
9. Pu, H.; Qiao, L.; Liu, Q.; Yang, Z.; Eur. Polym. J. **2005**, 41, 2505–2510.
10. Jouanneau, J.; Mercier, R.; Gonon, L.; Gebel, G. Macromolecules. **2007**, 40, 983-990.
11. Casella, L.; Monzani, E.; Gullotti, M.; Gliubich, F.; Gioia, L. D. J. Chem. Soc. Dalton Trans. **1994**, 3203-3210.