CHAPTER V
CONCLUSIONS

Two series of multi-benzimidazole structures were developed based on (i) the regular packing structures of the multifunctional benzimidazole model compounds (ii) flexible polymer stucture of multi-benzimidazole branching. In the case of the regular packing stucture, the mono- (**B-1**), di- (**B-2** and **B-3**)) and trifuctional (**B-4**) benzimidizoles clarifies that the number of benzimidazoles initiates different molecular packing stucture and hydrogen bond formation.The development of hydrogen bond patterns from a perpendicular hydrogen bond chain (as seen in **B-1**) and parallel hydrogen bond chain (as seen in **B-2** and **B-3**) under a lamella structure to a three dimensional columnar hydrogen bond chain (as seen in **B-4**) suggests the various packing structure based on the number of benzimidazole functional group in a single molecule. The temperature dependence FTIR allowed us to trace how intermolecular hydrogen bonds of each benzimidazole derivatives changed when the temperature was increased. **B-4** was found to maintain its packing structure which resulted in the highest proton conductivity of $7.8x10^{-2}$ S/cm at as high as 170 °C. In contrast, **B-3** hardly maintained its hydroden bond and showed the lowest proton conductivity of $9.2x10^{-3}$ at 170 °C as compared to the others.

Another type of benzimidazole designed in this work is the multi-benzimidazole branching polymer. The synthesis of this polymer was accomplished by simply applying branching polyethelenimine as a backbone and conjugating benzimidazoles onto the branches under various degree of substitution (%DS). It was found that the %DS was almost equal to the feed ratio which could be controlled in the range of 20%-91%. The proton conductivity was the most significant ($2x10^{-4}$ S/cm at 190 °C) when the %DS was about 20%. This information is important as it clarifies to us that although the hydrogen bond network is a key factor to motivate the proton transfer, the fact that the hydrogen bond reduced the chain mobility and as a consequence retarding the movement of benzimidazoles to transfer the proton, an optimal level of hydrogen bond with a certain level of chain mobility is necessary.

The present work also includes a molecular design and synthesis of a regular trifunctional benzimidazole pendant group containing in a polymer chain. The work accomplished the first part of the work, i.e., preparation of trifunctional benzimidazole pendant group. By applying nitromethanetripropionic acid chloride, the reaction with phenylenediamine quantitatively gives an intermediate tris[2-(benzimidazol-2-yl)ethyl]nitromethane which can be reduced to the final product of aminotris[2-(benzimidazol-2-yl)ethyl]methane.

The work to be done in the future is, for example, the conjugation of aminotris[2-(benzimidazol-2-yl)ethyl]methane on polyacrylic acid or other amino group containing linear polymers.