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A Stable Hydroxide-Conducting Polymer

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Supporting Information

ABSTRACT: A stable hydroxide-conducting membrane based on benzimidazolium hydroxide and its analogous anion-exchange polymer is reported for the first time. The molecular and polymeric analogues possess unprecedented hydroxide stability in neutral and KOH solutions as the soluble benzimidazolium salt, made possible by steric crowding around the benzimidazolium C2 position, which is usually susceptible to nucleophilic attack by OH^-. The polymers were cast and insolubilized for the purpose of forming membranes by blending with a poly(benzimidazole) followed by hydroxide-activated electrostatic interactions. The resulting membranes possess ionic (OH^-) conductivities of up to 13.2 mS cm^{-1} and represent a new class of anion-exchange polymers and membranes.

Alkali anion-exchange membranes are predominantly based on quaternary ammonium groups pendant to a polymer backbone.[1−7] The stability of quaternary ammonium groups is often poor in highly alkaline solutions, and thus, the performance of these materials has been shown to degrade rapidly over time.[8,9] There is a need to discover and explore positively charged polymers that offer the potential of improving the alkaline stability.

Despite the wealth of literature on positively charged benzimidazolium species (including an abundance of literature on ionic liquids), poly(benzimidazolium) analogues remain relatively unexplored. In recent publications, we[10] and Henkensmeier et al.[11] reported that anion-exchange materials can indeed be obtained by methylation of poly(benzimidazole) (PBI) and the resulting iodide ion exchanged for a chosen anion. However, our report, along with others in this area,[11,12] found that the hydroxide form of this polymer is unstable. In this report, we demonstrate that benzimidazolium hydroxide salts can be stabilized by steric crowding around the labile benzimidazolium C2 position and consequently use this strategy to synthesize novel polymers with greatly enhanced stability toward alkaline solutions. Moreover, a novel strategy for preparing insoluble membranes of these water-soluble polymers is reported.

The novel polymer reported herein, Mes-PBI (**1**), is a sterically crowded PBI synthesized from a tetraamine and a mesitylene-containing diacid. Dialkylation of the benzimidazole units with iodomethane affords poly[2,2′-(*m*-mesitylene)-5,5′-bis(*N*,*N*′-dimethylbenzimidazolium)] (Mes-PDMBI, **2-X**$^-$) in the iodide form (**2-I**$^-$). Subsequent ion exchange gives the hydroxide form **2-OH**$^-$, an alkali anion-exchange polymer (Figure 1).

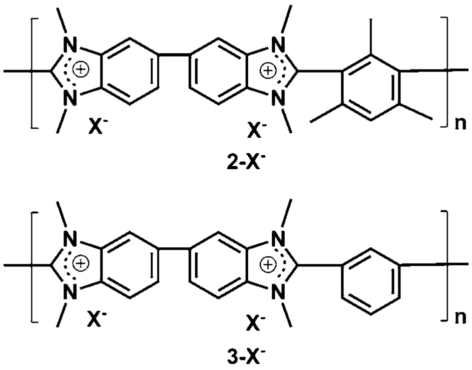

Figure 1. Poly[2,2′-(*m*-mesitylene)-5,5′-bis(*N*,*N*′-dimethylbenzimidazolium)] (Mes-PDMBI, **2-X**$^-$) and poly[2,2′-(*m*-phenylene)-5,5′-bis(*N*,*N*′-dimethylbenzimidazolium)] (PDMBI, **3-X**$^-$).

Stable benzimidazolium hydroxides are not known to exist. On the basis of reported hydroxide decomposition mechanisms of small-molecule benzimidazolium salts,[13−16] we envisioned that crowding around the reactive C2 position by installation of adjacent bulky groups would hinder nucleophilic attack by OH^-, thus improving the stability of the hydroxide form.

To examine this, we compared benzimidazolium salts **4** and **5** with a bulky mesityl group and a less-bulky phenyl group, respectively, attached at the C2 position. Computer models of these compounds (Figure 2a) predicted twisting of **4** that would result in juxtapositioned methyl groups sitting directly above and below the labile C2 position. In contrast, the phenyl-substituted analogue **5** was predicted to have the C2 carbon exposed (Figure 2b).

Compounds **4** and **5** were synthesized as shown in Scheme 1 [see the Supporting Information (SI) for full details]. The stabilities of these compounds were assessed spectroscopically upon their dissolution in alkaline solutions. Compound **4** was found to be stable in both 0.3 and 1.3 M aqueous KOH solutions; no change in the slightest was detected after 72 h of exposure. Compound **5**, on the other hand, was distinctly unstable, exhibiting half-lives of 1 h and <10 min in 0.3 and 1.3 M aqueous KOH, respectively (see the SI for details). The decomposition product of **5** (see Scheme 1), as determined by FTIR and ^1H NMR spectroscopy (see the SI for details), is consistent with OH^- attack at the C2 position of the benzimidazolium ring, thus confirming the hypothesis that shielding the C2 position should enhance the molecule's stability.

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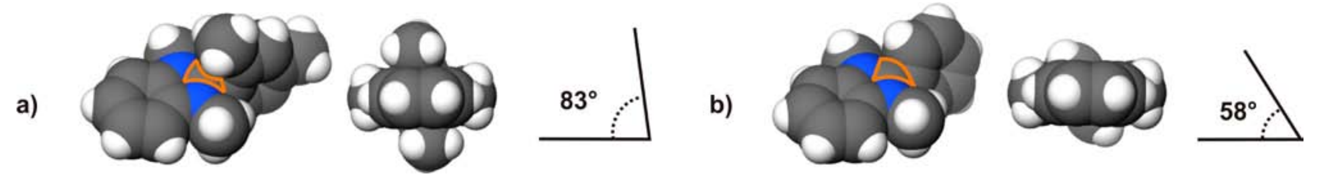
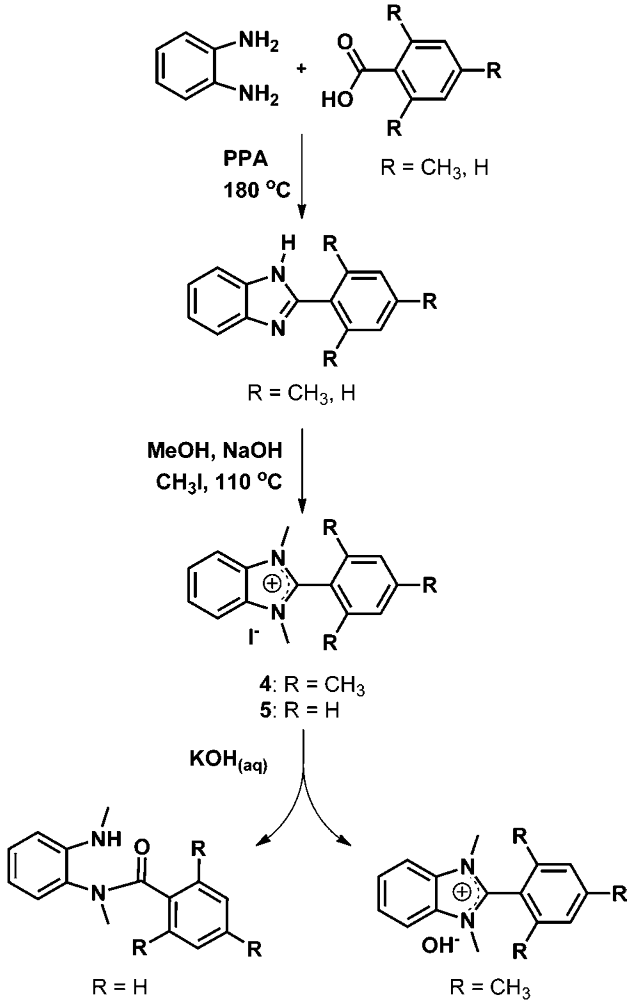
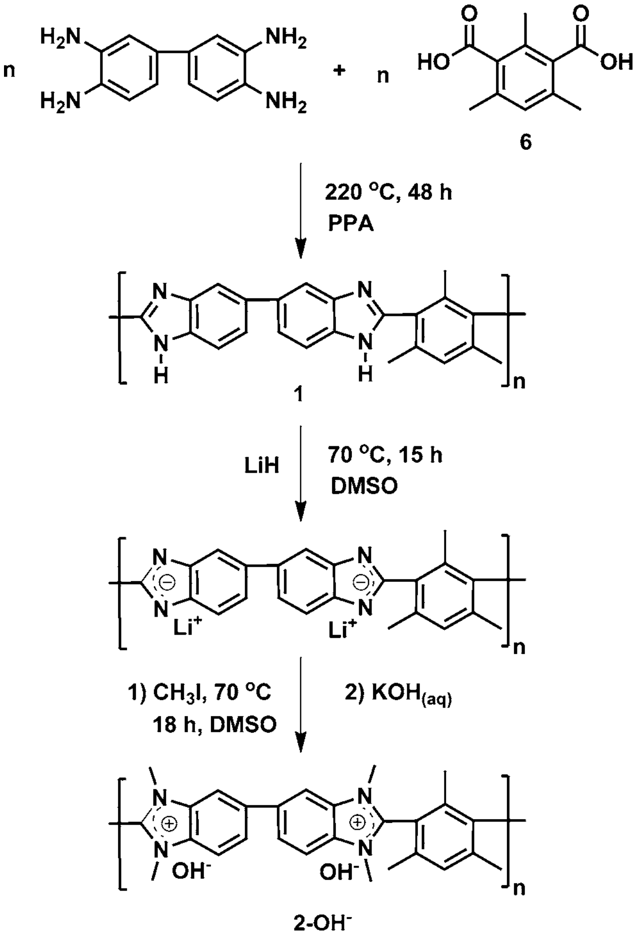


Figure 2. Simulation showing steric crowding around the C2 position and the dihedral angle of the inter-ring C−C bond for (a) **4** and (b) **5**. The C2 carbon is highlighted with an orange border for clarity.

Scheme 1. Synthesis of 2-Aryl-1,3-dimethylbenzimidazolium Compounds 4 and 5 and the Products (if Formed) upon Exposure to KOH Solution



Scheme 2. Synthesis of Mesitylene-Containing PBI 1 and Subsequent Dimethylation and Hydroxide Exchange To Form the Alkali Anion-Exchange Material 2-OH⁻

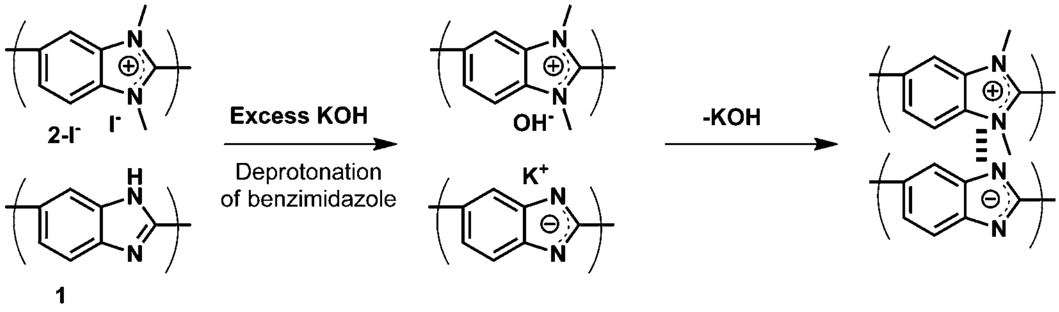


Satisfied with the stability of the hydroxide form of **4** in both alkaline solutions and the solid state, we synthesized the analogous polymer possessing a sterically crowded C2 position using a mesitylene-containing diacid monomer, 2,4,6-trimethylisophthalic acid (**6**), made in a four-step synthesis from bis(dichloromethyl)mesitylene (see the SI for details).[17,18] Polymerization of **6** with 3,3′-diaminobenzidine was carried out using modified literature procedures to produce polymer **1**.[19] **1** was subsequently methylated by deprotonation of the acidic protons using LiH followed by reaction with excess CH_3I (Scheme 2), resulting in polymer **2-I⁻** having a degree of methylation of >95%, as determined by ^1H NMR spectroscopy (see the SI for details).

Conversion of **2-I⁻** to **2-OH⁻** was achieved by soaking a film of **2-I⁻** in 0.5 M KOH(aq). During the conversion to the hydroxide form, the polymer film dissolved, which facilitated studies of the alkaline stability of **2-OH⁻** using ^1H NMR spectroscopy. In 2 M KOH(aq) at 60 °C over a period of 10 days, **2-OH⁻** showed no structural degradation within the experimental error of <1% (see the SI for details).

The water solubility of polymer **2-OH⁻** is a potential limitation in its application as a OH^- ion-exchange membrane. To prevent dissolution, we developed a novel strategy that utilizes the ability of PBIs to be converted into cationic and anionic forms. Membranes were prepared from blends of polymer **2** in the iodide form (**2-I⁻**) with lesser amounts of neutral **1**. Exposing the resulting blend membranes to basic solution removed the weakly acidic N−H protons in **1**, rendering the ring negatively charged (Scheme 3) and independently but simultaneously converting **2-I⁻** to **2-OH⁻**. Removal of excess KOH by washing rendered the film insoluble by virtue of the ionic interaction between the negatively

Scheme 3. Formation of Polymer−Polymer Ionic Interactions between Pairs of Positively Charged Benzimidazolium and Negatively Charged Benzimidazolide Rings Expected in Blends of Mes-PDMBI (2-X$^-$) and Mes-PBI (1) after Exposure to Aqueous KOH Solutions



charged benzimidazolide and positively charged benzimidazolium rings.

The resulting blend membranes had good mechanical properties, including tensile strength and strain at the break point in the fully hydrated state of 13 MPa and 28%, respectively. These values are comparable to those for other membranes reported in the literature[4,20] (experimental details are available in the SI). Although PBIs have been used extensively in the cross-linking of proton-exchange membranes,[21,22] they have not been used in this manner to cross-link anion-exchange membranes.

The ion-exchange capacity (IEC) of the membranes was controlled by varying the ratio of **2-I$^-$** to **1** in the original membrane (Table 1), keeping in mind the subtractive effect of acidic polymer **1** on **2-OH$^-$** after treatment with base and removal of excess KOH (the parent polymer **2-OH$^-$** had an IEC of 4.5 mmol g^{-1}). Blending with 25, 30, and 34% **1** decreased the IEC to 2.0, 1.5, and 1.0 mmol g^{-1}, respectively. The experimental values measured by back-titration matched the theoretical values calculated. The hydroxide stability of these blends was examined by monitoring the change in IEC over time for membranes soaked in 2 M KOH(aq) at 60 °C. The membranes were stable to within 5% of the original value after 13 days (see the SI for details).

Table 1. Properties of 1/2-OH$^-$ Blend Membranes[a]

1:2-OH$^-$ [b]	water uptake (wt %)	IEC (mmol g^{-1})[c]	λ[d]	σ_{OH^-} (mS cm^{-1})[e]
0:100	n/a[f]	4.5	n/a[f]	n/a[f]
25:75	162 ± 10	2.0	45	9.6 ± 0.1
30:70	119 ± 6	1.5	32	10.1 ± 0.1
34:66	82 ± 3	1.0	22	13.2 ± 0.1

[a] See the SI for experimental procedures. [b] Mass ratio of **1** to **2-OH$^-$** in the blend membrane. [c] Ion-exchange capacity. [d] H_2O/OH^- ratio. [e] Anionic conductivity measured at 21 °C, hydrated. [f] Not applicable due to membrane dissolution.

Preliminary measurements on nonoptimized membranes determined the conductivity to be in the 9−13 mS cm^{-1} range. This is in keeping with typical anion conductivities in hydrated membranes found in the literature, such as quaternary ammonium-substituted poly(aryl ether sulfone),[23] Nafion-based anion-exchange membranes,[24,25] and ionic-liquid-derived membranes,[26,27] but lower than those of the poly(phenylene)-based polymers described by Hibbs et al.[2] It is noted that the conductivity decreased with increasing IEC, which is common for membranes with high ion content, where excessive swelling and subsequent ion dilution lowers the conductivity.[28] Optimization of the blend ratios may offer even higher conductivities in these membranes.

In conclusion, a new anion-exchange material with hydroxide stability has been presented. The realization of the enhanced stability of this ubiquitous class of molecule, which results from reducing the access of OH$^-$ to the reactive C2 positions in the benzimidazole unit, creates new opportunities to prepare new benzimidazoles with unique or specialized properties. In addition, a novel and unique approach to ionic cross-linking has been demonstrated for PBIs that provides new opportunities to create novel ionic polymer blends.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Carrette, L.; Friedrich, K. A.; Stimming, U. *ChemPhysChem* **2000**, *1*, 162−193.

(2) Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromolecules* **2009**, *42*, 8316−8321.

(3) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187−200.

(4) Robertson, N. J.; Kostalik, H. A.; Clark, T. J.; Mutolo, P. F.; Abruna, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 3400−3404.

(5) Varcoe, J. R.; Slade, R. C. T.; Wright, G. L.; Chen, Y. L. *J. Phys. Chem. B* **2006**, *110*, 21041−21049.

(6) Varcoe, J. R.; Slade, R. C. T.; Yee, E. L. H.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. *Chem. Mater.* **2007**, *19*, 2686−2693.

(7) Chatenet, M.; Genies-Bultel, L.; Aurousseau, M.; Durand, R.; Andolfatto, F. *J. Appl. Electrochem.* **2002**, *32*, 1131−1140.

(8) Unlu, M.; Zhou, J.; Kohl, P. A. *Electrochem. Solid-State Lett.* **2009**, *12*, B27−B30.

(9) Vega, J. A.; Chartier, C.; Mustain, W. E. *J. Power Sources* **2010**, *195*, 7176−7180.

(10) Thomas, O. D.; Soo, K. J. W. Y.; Peckham, T. J.; Kulkarni, M. P.; Holdcroft, S. *Polym. Chem.* **2011**, *2*, 1641−1643.

(11) Henkensmeier, D.; Kim, H.-J.; Lee, H.-J.; Lee, D. H.; Oh, I.-H.; Hong, S.-A.; Nam, S.-W.; Lim, T.-H. *Macromol. Mater. Eng.* **2011**, *296*, 899−908.

(12) Henkensmeier, D.; Cho, H.-R.; Kim, H.-J.; Nunes Kirchner, C.; Leppin, J.; Dyck, A.; Jang, J. H.; Cho, E.; Nam, S.-W.; Lim, T.-H. *Polym. Degrad. Stab.* **2012**, *97*, 264−272.

(13) Schwarz, D. E.; Cameron, T. M.; Hay, P. J.; Scott, B. L.; Tumas, W.; Thorn, D. L. *Chem. Commun.* **2005**, 5919−5921.

(14) Pozharskii, A. F.; Kuz'menko, V. V.; Kashparov, I. S.; Sokolov, Z. I.; Medvedeva, M. M. *Chem. Heterocycl. Compd. (N. Y., NY, U. S.)* **1976**, *12*, 304−311.

(15) Bai, Y.-j.; Li, C.-y.; Sun, W.; Zhao, G.-f.; Shi, Z. *Huaxue Shiji* **2008**, *30*, 409−411.

(16) Hofmann, K. *Imidazole and Its Derivatives*; Interscience: London, 1953.

(17) Kolotuchin, S. V.; Thiessen, P. A.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Chem.—Eur. J.* **1999**, *5*, 2537−2547.

(18) Rhoad, M. J.; Flory, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 2216−2219.

(19) Ueda, M.; Sato, M.; Mochizuki, A. *Macromolecules* **1985**, *18*, 2723−2726.

(20) Zha, Y.; Disabb-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493−4496.

(21) Kerres, J.; Ullrich, A.; Meier, F.; Haring, T. *Solid State Ionics* **1999**, *125*, 243−249.

(22) Thomas, O. D.; Peckham, T. J.; Thanganathan, U.; Yang, Y.; Holdcroft, S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3640−3650.

(23) Yan, J.; Hickner, M. A. *Macromolecules* **2010**, *43*, 2349−2356.

(24) Salerno, H. L. S.; Beyer, F. L.; Elabd, Y. A. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 552−562.

(25) Jung, M.-s. J.; Arges, C. G.; Ramani, V. *J. Mater. Chem.* **2011**, *21*, 6158−6160.

(26) Ye, Y.; Elabd, Y. A. *Macromolecules* **2011**, *44*, 8494−8503.

(27) Lin, B.; Qiu, L.; Lu, J.; Yan, F. *Chem. Mater.* **2010**, *22*, 6718−6725.

(28) Peckham, T. J.; Holdcroft, S. *Adv. Mater.* **2010**, *22*, 4667−4690.