N-Spirocyclic Quaternary Ammonium Ionenes for Anion-Exchange Membranes

Thanh Huong Pham, Joel S. Olsson, and Patric Jannasch*

Polymer & Materials Chemistry, Department of Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

S *Supporting Information*

ABSTRACT: The development of cationic polymers for anion-exchange membranes (AEMs) with high alkaline stability and conductivity is a considerable challenge in materials chemistry. In response, we here present the synthesis and properties of N-spirocyclic quaternary ammonium ionenes (spiro-ionenes) containing 5- and 6-membered rings fused by central nitrogen cations. High-molecular weight and film-forming spiro-ionenes are successfully synthesized in cyclo-polycondensations of tetrakis(bromomethyl)benzene and dipiperidines under mild conditions. These polyelectrolytes show excellent thermal and alkaline stability with no degradation detected by NMR spectroscopy after more than 1800 h in 1 M KOD/D_2O at 80 °C. Even at 120 °C, the spiro-ionenes display reasonable alkaline stability. Transparent and mechanically robust AEMs based on ionically cross-linked blends of spiro-ionene and polybenzimidazole reach OH^- conductivities up to 0.12 S cm^{-1} at 90 °C. The current findings demonstrate that spiro-ionenes constitute a new class of alkali-stable anion-exchange polymers and membranes.

The development of anion-exchange membranes (AEMs) which combine long-term stability and high hydroxide ion conductivity in alkaline electrochemical systems is currently an intensive area of materials research.[1] In general, these membranes are based on polymers tethered with quaternary ammonium (QA) cations.[1] Because of its highly basic and nucleophilic nature, the hydroxide ion is prone to attack and degrade archetypal QA and other cationic groups via, e.g., Hofmann eliminations and nucleophilic substitutions.[2] In addition, polymer backbones may degrade via, e.g., cleavage of activated ether bridges.[3] Consequently, the hydroxide ion conductivity and mechanical properties of AEMs normally deteriorate over time. This severely limits their applicability, especially at temperatures above 60 °C.

Successful strategies used to improve the alkaline stability of cationic groups include the utilization of steric protection,[2d,4] conformational restrictions,[5] inductive effects[6] and metal complexes.[7] Recently, Marino and Kreuer reported on the exceptional alkaline stability of certain N-spirocyclic QA salts, especially 6-azonia-spiro[5.5]undecane.[5a] The high stability of the six-membered spirane ring system was ascribed to the constrained ring conformation which increases the transition state energy of both substitution and elimination reactions.[5a]

Introducing N-spirocyclic QA cations into polymers presents a significant challenge and calls for new synthetic pathways.[5b] Using a straightforward approach, we have in the present work molecularly designed and synthesized ionenes via cyclo-polycondensations in which spiro-centered QA cations are formed directly in the polymer backbone. As shown in Figure 1,
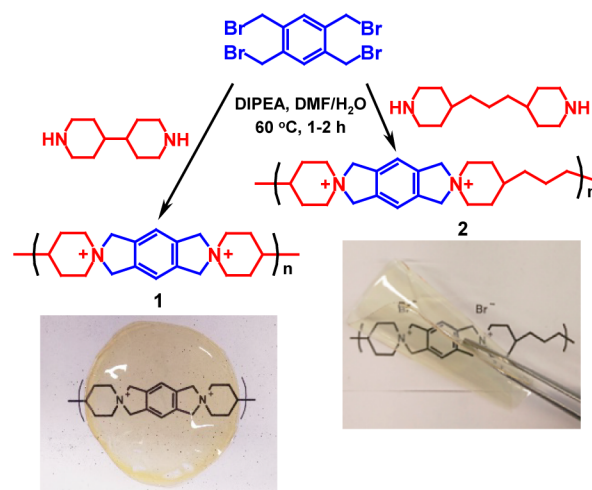

Figure 1. Synthetic pathway to spiro-ionenes **1** and **2** via cyclo-polycondensation of 4BMB with BP and TMDP, respectively, and photographs of their films cast from water solutions at 120 °C.

these "spiro-ionenes" lack both ether linkages and strongly electron drawing groups. Although Müllen et al. reported on a similar polymer already in 1990, only the solubility and the thermal properties have been disclosed.[8] In the current work, we synthesized two novel spiro-ionenes from commercially available building blocks. Hence, tetrakis(bromomethyl)-benzene (4BMB) was employed in straightforward cyclo-polycondensations with two commercially available dipiper-idines, 4,4′-bipiperidine (BP) and 4,4′-trimethylenedipiperidine (TMDP), to form spiro-ionene **1** and **2**, respectively (Figure 1). 4BMB was synthesized in-house in order to obtain a high-purity material (see Supporting Information). The polymerizations were carried out in N,N-dimethylformamide/water mixtures at 60 °C, using N,N-diisopropylethylamine (DIPEA) as catalyst.

In the two-step cyclization reaction, a deprotonated piperidine nitrogen first makes an intermolecular nucleophilic attack on one of the benzylic carbons of 4BMP, followed by a

ring-forming intramolecular quaternization involving the neighboring benzyl bromide (Scheme S1). Despite potential side reactions, the desired intramolecular cyclization reaction leading to chain growth was found to dominate completely. The monomer concentration of the reaction mixture was kept low, resulting in final polymer concentrations of 1.5−3 wt %. Still, the polycondensations gave high-molecular weight products in quantitative yields within 1−2 h without any signs of side-reactions. This clearly demonstrated the high specificity and efficiency of the polymerization.

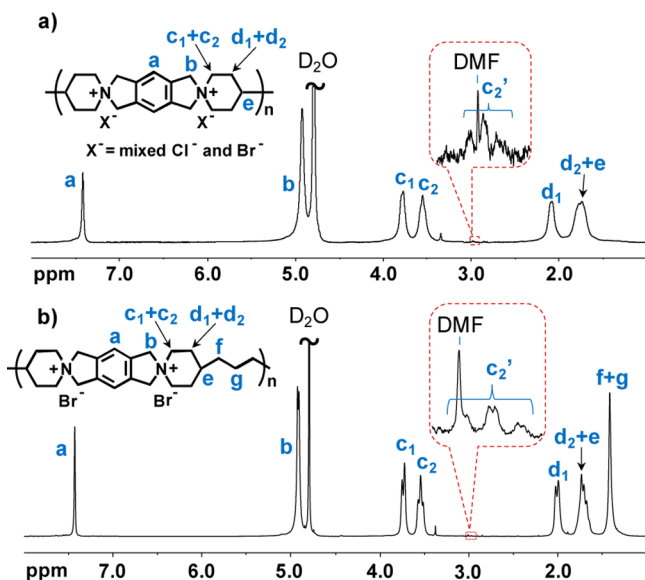The ^{1}H NMR spectra of the spiro-ionenes shown in Figure 2 revealed that the equatorial and axial protons at α and β

Figure 2. ^{1}H NMR spectra of (a) spiro-ionene **1** and (b) spiro-ionene **2** (chain end-group signals are enlarged).

positions in the piperidinium moiety displayed a large difference in chemical shifts, leading to splitting of each position into two distinct signals (c_1 and c_2, and d_1 and d_2, respectively). This demonstrated the rigid structure and slow conformational changes of the spirocyclic system. All the shifts in the spectra confirmed the desired ionene structures. By comparing the intensities of the signals originating from the piperidinium end groups (c_2') and the N-spirocyclic QA groups (c_2), the number-average molecular weight (M_n) of spiro-ionene **1** and **2** was calculated as 67 and 80 kg mol^{-1}, respectively (the intensity of c_2' was corrected by taking into account the DMF signal at 2.8 ppm). Additionally, the intrinsic viscosity ($[\eta]$) in H$_2$O was measured to be 0.40 and 0.56 dL g^{-1}, respectively (Table S1). The ion exchange capacity (IEC, meq g^{-1}) of the spiro-ionenes was determined by Mohr's titration. In the case of **2**, the titrated IEC was in complete agreement with the theoretical IEC (4.0 mequiv g^{-1}, Table S1). From the synthesis, **1** contained a mix of Br$^-$ and Cl$^-$ counterions. Hence, the theoretical IEC was calculated as a span, 4.4−5.4 mequiv g^{-1}, to be compared with the titrated IEC of 4.6 mequiv g^{-1}, Table S1.

In spiro-ionene **1**, the stiff segments with the five interconnected rings were directly linked via single C−C bonds in the backbone. In contrast, spiro-ionene **2** contained flexible −(CH$_2$)$_3$− spacer chains in-between the rigid ring moieties. As expected, the chain flexibility had a direct impact on the properties of the resulting ionenes. For example, the stiff

chain structure of spiro-ionene **1** reduced the solubility in relation to **2**. Consequently, it was necessary to use a higher water content during the polymerization of **1**. Although **2** was readily soluble in dimethyl sulfoxide at room temperature, **1** did not dissolve in this solvent even at 80 °C. Both ionenes were readily soluble in methanol and water, but did not dissolve in the polar aprotic solvents N-methyl-2-pyrrolidone and dimethylacetamide.

As shown in Figure 1, the spiro-ionenes formed light yellow, transparent and flexible films when cast from 5 wt % aq. solutions at 120 °C. The water uptake of the spiro-ionene **1** film reached 27 and 68 wt % at 55 and 93% relative humidity (RH), respectively, after 48 h of equilibration at room temperature (Figure S5). Under the same conditions, spiro-ionene **2** took up 17 and 44 wt % water, respectively. The lower water uptake of the latter film may be explained by its lower ionic content. Spiro-ionene films were analyzed by small-angle X-ray scattering (SAXS) in order to study structure formation (Figure S7). After equilibration at 75% RH, **2** showed a weak ionomer peak at $q_{max} \sim 4.8$ nm^{-1}, corresponding to a characteristic distance of $d \sim 1.3$ nm. This distance was in the same range as the length between two neighboring ionic centers via an extended trimethylene spacer (~ 1.1 nm). In contrast, no ionomer peak was observed for **1**, possibly because of the much stiffer structure and shorter interionic distance (~ 0.7 nm) prevented the formation of a distinct morphology on the nm level.

Thermogravimetrical analysis (TGA) revealed a high thermal stability with decomposition only well above 300 °C under N$_2$ (Figure S4). Spiro-ionene **1** showed a higher thermal decomposition temperature ($T_{d,95}$) than **2**, presumably because of the stiffer structure and higher degree of aromaticity of the former. Alkaline stability is a critical property for applications of AEMs that determines the lifetime of electrochemical devices such as fuel cells and electrolyzers.[1a] Here, the spiro-ionenes were dissolved in 1 M KOD in D$_2$O and kept at 80 and 120 °C, respectively, before analysis by ^{1}H NMR spectroscopy. Figure 3 displays selected spectra of the two samples before and after storage at 80 and 120 °C (all spectra are provided in Figure S9−S12).

The high pH and temperature of the solutions facilitated proton−deuterium (H-D) exchanges at benzylic and aromatic positions. H-D exchange at the benzylic positions resulted in disappearance of the corresponding signals within 168 h at 80 °C (Figure 3). At 120 °C, both the aromatic and benzylic signals disappeared within 72 h. As expected, these exchanges were reversible. After treatment in 1 M KOH in H$_2$O at 120 °C during 72 h, the labile deuterium atoms were exchanged back to protons, resulting in the increase of the intensities of the corresponding ^{1}H NMR signals (Figure S13). Besides effects of H-D exchange, the ^{1}H NMR spectra of both spiro-ionenes showed no detectable changes after 672 h storage in 1 M KOD/D$_2$O at 80 °C, indicating a very high alkaline stability at this temperature (Figure 3). Spiro-ionene **2** was even kept for 1896 h without any noticeable signs of structural degradation (Figure S10). However, at 120 °C the spectra of both samples revealed distinct signs of degradation as new signals appeared and increased in intensity over time (Figure S11 and S12).

Each cation in the spiro-ionenes is the center of a spirocyclic system of one 5- and one 6-membered ring. Because of higher ring strain, the former ring is more susceptible to alkaline attack.[5a] In addition, the presence of the fused benzene ring can be expected to further destabilize the 2 and 4 (benzylic)
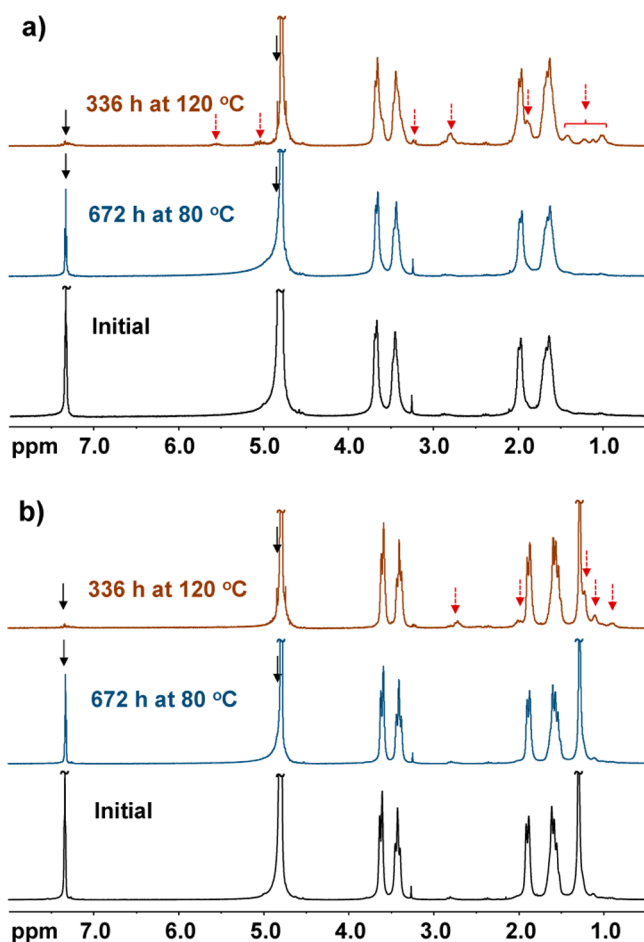
Figure 3. ^{1}H NMR spectra of (a) spiro-ionene **1** and (b) **2** before and after storage in 1 M KOD/D$_2$O during 672 and 336 h at 80 and 120 °C, respectively (black and red arrows indicate changes in the spectra due to H−D exchange and degradation, respectively).

positions of the 5-membered ring. This favors ring-opening substitution at these positions as the dominating degradation pathway (Scheme S2a). The ^{1}H NMR spectrum of spiro-ionene **2** recorded after 336 h at 120 °C confirmed this. The new signals emerging at ~2.7 and 2.0 ppm consisted of a doublet and a triplet, respectively, with a coupling constant of $J \sim 12$ Hz. This corresponded well with the axial and equatorial α-protons in 1-benzyl-4-methylpiperidine.[9] Further signals appearing at ~1.1, 1.0 and 0.9 ppm may arise from additional aliphatic protons in the degraded trimethylene bipiperidine moiety. Assuming that ring-opening substitution was the only active degradation reaction, the degree of degradation was estimated by comparing the intensity of the new signal at ~2.7 ppm and the original spiro-ionene signal at ~3.6 ppm in the same spectrum. This suggested a loss of a mere ~10% of the cations of **2** after 336 h at 120 °C.

After storage at 120 °C, multiple new signals emerged in the ^{1}H NMR spectra of spiro-ionene **1** to indicate a much more complex degradation process than for **2** (Figure 3). Signals emerging at ~2.8 and 1.9 ppm may imply ring-opening substitution at the 5-membered ring (Scheme S2a). However, the appearance of at least four broad signals, instead of the expected two, between 1.4 and 1.0 ppm suggested that ring-opening substitution at the 6-membered ring may also have occurred (Scheme S2b). Based on the intensity ratio between the signals at ~2.8 and 3.7 ppm, arising from α-protons in the

original and the degraded piperidinium moiety, respectively, the degradation via 5-membered ring opening substitution was estimated to be ~15% after 336 h at 120 °C. Furthermore, the relatively weak multiplets at ~5.5 and 5.0 ppm corresponded well with the shifts of alkene (=CH$_2$) and alkenyl (—CH= CH$_2$) protons, clearly suggesting degradation via ring-opening elimination (Scheme S2c). The degradation via this route was estimated to be ~10% from the intensity ratio of the signals at 5.5 and 3.7 ppm. Still, the total loss of cations was most probably higher due to additional degradation reactions. A possible explanation for the markedly higher stability of spiroionene **2**, in comparison to **1**, may be that the flexible trimethylene bridges in the former greatly facilitate ring strain relaxation. This is likely to mitigate the distortion of the 6-membered ring system, which is necessary during the degradation reaction.[4a]

To employ water-soluble polymers as AEMs practically, they need to be efficiently immobilized to prevent dissolution. In the present case, we developed novel blend membranes containing spiro-ionene **2** and a commercially available polybenzimidazole (PBI-OO) to demonstrate the possibility to prepare water insoluble and highly hydroxide ion conductive AEMs based on spiro-ionenes. Blend membranes containing 70, 75 and 80 wt % spiro-ionene **2**, respectively, were cast at 65 or 80 °C from 5 wt % solutions of the polymers in dimethyl sulfoxide (Table S2). The resulting membranes, denoted S70P30, S75P25 and S80P20, respectively, were brown-yellow, transparent and flexible (Figure 4a), and decomposed only above 350 °C
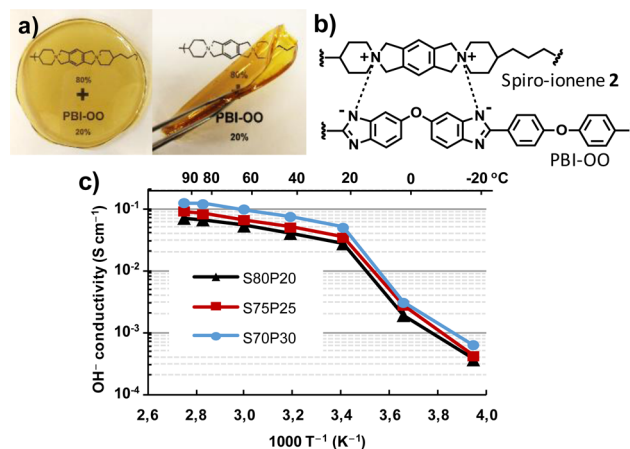

Figure 4. (a) Photographs of blend AEM S80P20 indicating excellent transparency and foldability. (b) Scheme of the ammonium-imidazolate complexes formed by spiro-ionene **2** and PBI-OO in the water insoluble blend AEMs. (c) Arrhenius OH$^-$ conductivity plots of blend membranes S80P20, S75P25 and S70P30 fully immersed in water (the sharp increase of conductivity up to 20 °C was caused by ice melting).

(Figure S4). Treatment of these membranes in 0.5 M aqueous KOH solution exchanged the counterion of the spiro-ionene to OH$^-$. In addition, at least a part of the −NH− groups of PBI-OO were deprotonated to enable the formation of ammonium-imidazolate complexes between the spiro-ionene and PBI-OO (Figure 4b). This resulted in completely water-insoluble and flexible AEMs, as long as kept under basic conditions.

SAXS profiles of the blend AEMs were very similar to that of the neat spiro-ionene **2** (Figure S7). The water uptake of the AEMs in the OH$^-$ form was found to increase with temperature

and spiro-ionene content (Figure S6). At 20 °C membrane S70P30 and S80P20 took up just above 100 and 450 wt % water, respectively. Despite the high water uptake, the membranes remained intact and did not disintegrate. Figure 4c shows the OH^- conductivity of the AEMs fully immersed in water. As shown, membrane S80P20, S75P25 and S70P30 reached 27, 34 and 49 mS cm^{-1}, respectively, at 20 °C. At 90 °C, the conductivity of the same membranes had risen to very high values: 70, 90 and 120 mS cm^{-1}, respectively. Notably, the conductivity increased with decreasing spiro-ionene content and water uptake. This is typically observed for highly water-swollen membranes where the dilution of charge carries leads to limitations of the conductivity.[10] It implied that even higher conductivity values may be reached after further blend optimization.

In conclusion, high-molecular weight ionenes with a spirane structure were synthesized via cyclo-polycondensations under mild conditions using commercially available precursors. The restricted ring system induced an excellent thermal and alkaline stability, and both spiro-ionenes remained intact over at least 672 h in 1 M KOD/D_2O at 80 °C, with a reasonable stability also at 120 °C. The applicability of these ionenes was shown by the preparation of highly OH^- conductive AEMs based on ionic blends with polybenzimidazole. The results demonstrate that spiro-ionenes constitute a new class of unique alkali-stable anion-exchange polymers and membranes. Our future work will focus on the separation of the spiro-centered QA cations along the ionenes to reduce the ionic content and water uptake of these materials while retaining their high conductivity.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12944.

> Detailed experimental descriptions; TGA, water uptake, SAXS data; additional ^1H NMR spectra from the alkaline stability study (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*patric.jannasch@chem.lu.se

ORCID ⓘ

Patric Jannasch: 0000-0002-1102-3959

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T.; Zhuang, L. *Energy Environ. Sci.* **2014**, *7*, 3135. (b) He, G.; Li, Z.; Zhao, J.; Wang, S.; Wu, H.; Guiver, M. D.; Jiang, Z. *Adv. Mater.* **2015**, *27*, 5280. (c) Wang, Y. J.; Qiao, J. L.; Baker, R.; Zhang, J. *J. Chem. Soc. Rev.* **2013**, *42*, 5768. (d) Merle, G.; Wessling, M.; Nijmeijer, K. *J. Membr. Sci.* **2011**, *377*, 1. (e) Couture, G.; Alaaeddine, A.; Boschet, F.; Ameduri, B. *Prog. Polym. Sci.* **2011**, *36*, 1521. (f) Li, N.; Guiver, M. D. *Macromolecules* **2014**, *47*, 2175.

(g) Hickner, M. A.; Herring, A. M.; Coughlin, E. B. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 1727.

(2) (a) Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C* **2008**, *112*, 3179. (b) Edson, J. B.; Macomber, C. S.; Pivovar, B. S.; Boncella, J. M. *J. Membr. Sci.* **2012**, *399−400*, 49. (c) Macomber, C. S.; Boncella, J. M.; Pivovar, B. S.; Rau, J. A. *J. Therm. Anal. Calorim.* **2008**, *93*, 225. (d) Mohanty, A. D.; Bae, C. *J. Mater. Chem. A* **2014**, *2*, 17314.

(3) (a) Chen, D.; Hickner, M. A. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5775. (b) Mohanty, A. D.; Tignor, S. E.; Krause, J. A.; Choe, Y. K.; Bae, C. *Macromolecules* **2016**, *49*, 3361. (c) Arges, C. G.; Ramani, V. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 2490.

(4) (a) Thomas, O. D.; Soo, K. J.; Peckham, T. J.; Kulkarni, M. P.; Holdcroft, S. *J. Am. Chem. Soc.* **2012**, *134*, 10753. (b) Hugar, K. M.; Kostalik, H. A.; Coates, G. W. *J. Am. Chem. Soc.* **2015**, *137*, 8730.

(5) (a) Marino, M. G.; Kreuer, K. D. *ChemSusChem* **2015**, *8*, 513. (b) Pham, T. H.; Jannasch, P. *ACS Macro Lett.* **2015**, *4*, 1370. (c) Dang, H.-S.; Jannasch, P. *J. Mater. Chem. A* **2016**, *4*, 11924. (d) Yang, Z.; Guo, R.; Malpass-Evans, R.; Carta, M.; McKeown, N. B.; Guiver, M. D.; Wu, L.; Xu, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 11499.

(6) (a) Lee, W.-H.; Kim, Y. S.; Bae, C. *ACS Macro Lett.* **2015**, *4*, 814. (b) Yang, Z.; Zhou, J.; Wang, S.; Hou, J.; Wu, L.; Xu, T. *J. Mater. Chem. A* **2015**, *3*, 15015. (c) Liu, Y.; Zhang, B.; Kinsinger, C. L.; Yang, Y.; Seifert, S.; Yan, Y.; Mark Maupin, C.; Liberatore, M. W.; Herring, A. M. *J. Membr. Sci.* **2016**, *506*, 50. (d) Dang, H. S.; Weiber, E. A.; Jannasch, P. *J. Mater. Chem. A* **2015**, *3*, 5280.

(7) (a) Mao, C.; Kudla, R. A.; Zuo, F.; Zhao, X.; Mueller, L. J.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2014**, *136*, 7579. (b) Zha, Y.; Disabb-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493.

(8) Müllen, K.; Lex, J.; Schulz, R. C.; Walter, F. *Polym. Bull.* **1990**, *24*, 263.

(9) Cano, R.; Yus, M.; Ramon, D. J. *Tetrahedron* **2011**, *67*, 8079.

(10) (a) Marino, M. G.; Melchior, J. P.; Wohlfarth, A.; Kreuer, K. D. *J. Membr. Sci.* **2014**, *464*, 61. (b) Peckham, T. J.; Holdcroft, S. *Adv. Mater.* **2010**, *22*, 4667.