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ARTICLE

The Role of Anions on Light-Driven Conductivity in Diarylethene-Containing Polymeric Ionic Liquids

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Polymeric ionic liquids (PILs) with light-driven conductivity represent a new class of smart materials with potential applications as soft electronics, however the influence of counterion characteristics on their conducting properties remains unexplored. We synthesized a series of PILs based on copolymers of ethylene oxide and allyl glycidyl ether with different anions and light responsive imidazolium-containing diarylethene (DAE) cations. This study shows that anion character impacts the photostationary state (PSS), magnitude of conductivity, and light responsive properties of PILs. Compared with BF_4^-, anions featuring stronger cation-anion interaction (I^-) and higher ratio of the ring-closed isomer at PSS ($TFSI^-$) have a larger impact on the degree of change in ionic conductivity upon light irradiation. With this versatile synthetic platform, the electronic properties of the DAE cations can be non-invasively modulated by light with minimal structural change, providing the ability to study, *in-situ*, cation-anion interaction without competing effects that arise from changes in polymer T_g or counterion size. These results are beneficial for understanding ion transport and structural design of smart light-responsive PILs.

Introduction

Functional materials translating light energy into tunable ion conduction drive a variety of useful processes, from light-gated ion channels[1] and nanoporous membranes[2] to controlling ion transport in halide perovskites.[3] Compared to other stimuli used to control ion conduction, light offers inherent advantages due to the possibility to instantly turn the signal on or off, to create complex spatial patterning, and to vary the wavelength.[4] Moreover, it does not require physical contact with the photoresponsive substance, enabling remote control. All of these advantages have inspired the development of smart devices, such as light-controlled electrical circuits and wearable photodetectors. Polymeric ionic liquids (PILs) are a particularly interesting class of ion conducting materials due to their tailorable polymer architecture, high thermal and chemical stability, mechanical durability and the possibility of tuning both conductivity and mechanical properties through metal-ligand coordination.[5–7] However, a current challenge is to design PIL-based systems that enable these properties to be modulated with light.[8–11]

Yan, Wu, Huang and co-workers developed a hydrogel with reversible photocontrolled conductivity based on photoresponsive host-guest interaction between cyclodextrin host and azobenzene or ionic liquid guest that are able to modulate the concentration of free-moving ions within the gel matrix.[8] Because azobenzene has a large conformational change upon E/Z photoisomerization, the host-guest pair readily undergoes complexation and decomplexation under irradiation. More recently, our team reported a new type of photoresponsive PIL using imidazolium-containing diarylethenes (DAEs) as ionic pendant groups covalently attached to a poly(ethylene oxide) backbone.[9] The photoinduced changes in electronic properties of DAE salts modulate the binding between anions and imidazolium containing DAE cations, and thus the ionic conductivity of the PIL solid films. Although these examples demonstrate that conformational and electronic changes in photoswitchable molecules can enable tunable ion conduction in PILs, an understanding of the influence of cation/anion characteristics on light responsive conductivity remains unexplored. In contrast, previous studies on the conductivity of traditional non-photoresponsive PILs revealed that many factors such as cation-anion interactions, polymer glass transition temperature T_g, and molar volume of counterions all influence the macroscopic physicochemical properties.[12] For example, Runt and coworkers have observed that the T_g independent ionic conductivities of PILs with different anions spanned more than three orders of magnitude.[13] Huck and coworkers have also shown the wetting properties of substrates modified with cationic polyelectrolyte brushes are strongly dependent on the nature of the counterion.[14] Thus, it is essential to understand the influence of the cation/anion on ionic conductivity and their

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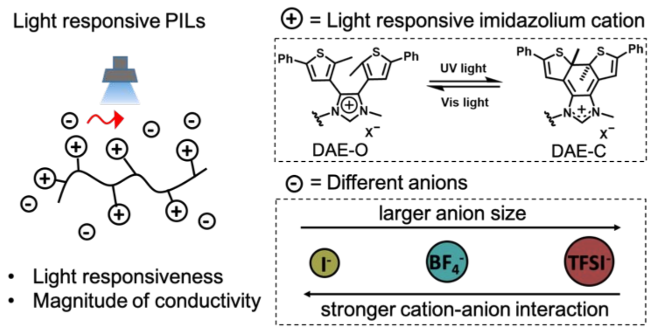


Figure 1. PILs based on imidazolium containing DAE cations, and effect of anions on the magnitude and light responsiveness of their ionic conductivity.

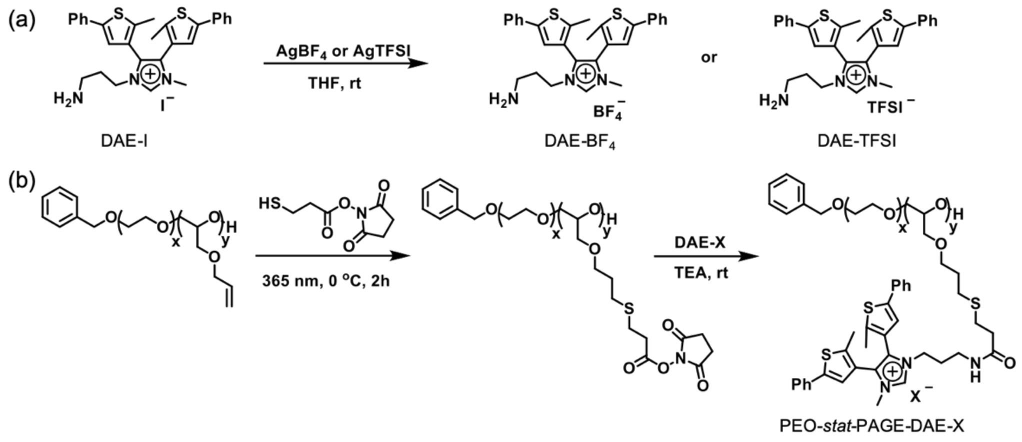
changes with light stimulus in order to design high-performance light-responsive PIL materials.

This study examines the impact of anion properties on ion conductivity in light responsive DAE-containing PILs by systematically changing the size of the anion (Figure 1). This versatility enables the direct study of how characteristics of the counterion impact photostationary state (PSS), which defines the equilibrium composition of ring-open isomers and ring-closed isomers with UV light irradiation, magnitude of conductivity and light responsive properties, without the addition of additives. This work finds that anion identity, I^- leads to stronger cation-anion interaction, and $TFSI^-$ leads to higher ratio of the ring-closed isomer at the PSS than BF_4^-. These features result in a larger change in ionic conductivity upon light irradiation. In addition, this versatile synthetic platform provides the ability to study, *in-situ*, cation-anion interaction without competing effects that arise from changes in polymer T_g or counterion size. Importantly, this work lays the foundation for structural design of smart light-responsive PILs.

Results and discussion

To elucidate the effect of ionic structure on the light responsive ion conducting properties of PILs, a series of anions (I^-, BF_4^-, $TFSI^-$) were incorporated into statistical copolymer of ethylene oxide and allyl glycidyl ether (PEO-*stat*-PAGE) (ca. 10 mol% AGE) with the imidazolium-containing DAEs as covalently attached cation.[15] The synthesis of DAE-I bearing reactive primary amines for attachment to the polymer backbone was adapted from previous work (Scheme 1).[16] To obtain reactive DAE salts with different anions (DAE-BF_4, DAE-TFSI) of interest, anion metathesis was performed. The synthesis of the DAE-functionalized PEO-*stat*-PAGE polymer (PEO-*stat*-PAGE-DAE-X) is based on a combination of thiol–ene click reaction and N-hydroxysuccinimidyl ester strategy.[9] The T_g of the resulting PILs with I^-, BF_4^-, and $TFSI^-$ are -5, 0, and 0 °C respectively (Figure S1). Significantly, this post-functionalization method enables the effect of the anion identity on T_g and ionic conductivity to be studied without interference from polymer backbone properties, such as molecular weight or dispersity. As the anion identity can affect the molecular weights or average chain lengths of the polymers obtained via direct polymerization of imidazolium salts containing monomers in some previous studies, it is a challenge to obtain polymers with the same backbone structures, which influences the conductivity and T_g.[17] In addition, with this synthetic approach, no anion exchange is required, which alleviates issues arising from incomplete anion exchange, solubility change, and requirement of time consuming dialysis process.[18]

Counteranions with significantly different sizes were chosen for PEO-*stat*-PAGE-DAE-X, giving access to PILs featuring tunable cation-anion electrostatic interaction. The ion radii of I^-, BF_4^-, and $TFSI^-$ are 2.25, 3.44, and 4.39 Å respectively.[19,20] For imidazolium based ionic liquids[21] and polymeric ionic liquids,[22] it is reported that larger counter ion size leads to weaker ion associations due to charge delocalization. As a first screening of the different nature of the DAE derivatives and their corresponding PILs, ^1H NMR measurements were carried out using the downfield chemical shift of the C2 proton of the imidazolium ring as an indication of the stronger cation-anion interaction.[23–26] It is noted that C2 protons of DAE-X and PEO-*stat*-PAGE-DAE-X show anion-dependent chemical shifts in inert solvents, such as $CDCl_3$ or CD_2Cl_2, which are considered to represent the intrinsic properties of the solute (Figure 2 and Figure S2).[27] As anticipated, the peaks shift towards lower ppm



Scheme 1. (a) Synthesis of primary amine functionalized imidazolium containing DAE salts with different anions; (b) Synthesis of PILs PEO-*stat*-PAGE-DAE-X (I, BF_4, TFS

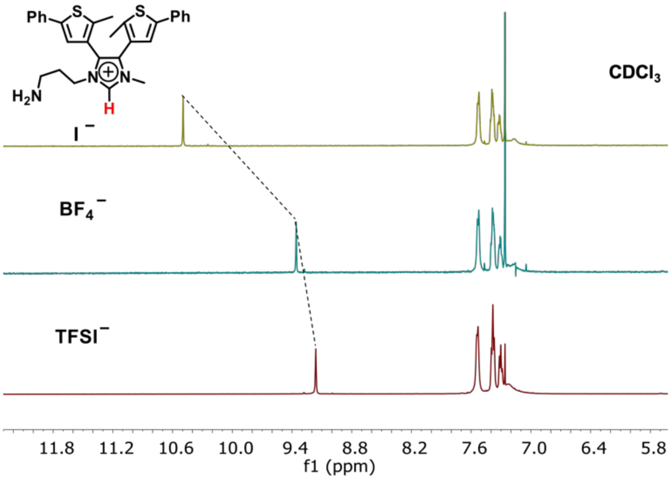


Figure 2. ^{1}H NMR of DAE-X (I^-, BF_4^-, $TFSI^-$), and the high field chemical shift of C2 proton indicating weaker cation-anion interactions.

values when going from small, basic, and strongly coordinating anions to larger, less basic, and weaker coordinating anions. In addition, a significant decrease in chemical shifts is observed from I^- to BF_4^-, while BF_4^- and $TFSI^-$ feature similar values, confirming that both BF_4^- and $TFSI^-$ anions have lower basicity and coordination strength compared to I^-. This is in agreement with previously published ^{1}H NMR data of imidazolium containing PILs by the Lokitz group.[22]

With PEO-*stat*-PAGE-DAE-X, the electron density of the central imidazolium ring of DAE units can be reversibly modulated using two different wavelengths of light. This electron density change results in a stronger association of the anions and thus lower ionic conductivity with the ring-closed DAE isomer than the ring-open DAE isomer.[9] To understand the impact of anions on the photoswitching properties of PEO-*stat*-PAGE-DAE-X, a series of pump–probe UV-Vis experiments were carried out. The photoswitching properties of DAE-X and PEO-*stat*-PAGE-DAE-X are compared in both solution and solid films. The solution studies provide extinction coefficients while the solid-state experiments are more similar to systems employed for actual conductivity measurements. As expected, all the DAE-X and PEO-*stat*-PAGE-DAE-X derivatives underwent reversible photochromic reactions, albeit with a small amount of degradation during the light irradiation.[28] In these systems, irradiation with UV light (300 nm) triggers photocyclization of the DAE units to generate the ring-closed isomer (Figure S4, S5). According to density functional theory (DFT) calculations, the enthalpy difference between the ring-open to closed form is 26.6 kcal/mol (Figure S6, S7). The difference in the energies of the isomers was comparable to those recently reported for dithienylbenzene (26.5 kcal/mol).[29] These studies corroborate that the induced positive charge on the imidazolilum ring does not significantly affect the energy difference. Also, this isomerization reaction is characterized by a strong shift in absorption from colorless to blue through the formation of extended π-conjugation in the ring-closed isomer.[16] DFT studies also revealed that the ring-closed isomer induces a planarized geometry while the backbone of the ring-open isomer shows a twisted structure. Thus, the planar backbone resulted in π-conjugation throughout the DAE unit and red-shifted spectra (Fig S8, S9). The blue colored ring-closed isomer can be reversed back to its initial state upon irradiation with visible light. Consistent with other classes of DAE-based photoswitches, thermal reversion to the ring-open isomer can occur in the dark.[4,30] We note that although the reversion back to ring-open isomer can occur in the dark, the time needed to induce the thermal back reaction is much greater (>8 h) than that needed to conduct studies on light-driven conductivity in the PILs (Figure S10). The half-life and activation energy of ring-closed to ring-open thermal relaxation of DAE units attached on polymer in solid state are measured and summarized (Table S2, Figure S11, S12). Thus photoswitching, and not thermal relaxation, is predominately responsible for the reformation of the ring-open isomer and change in conductivity under visible light illumination. The conversion ratios from ring-open isomer to ring-closed isomer at the PSS with UV light (λ = 300 nm) in CH_3CN by ^{1}H NMR are 70, 70, and 82% for I^-, BF_4^-, and $TFSI^-$ respectively (Figure S3). The values of the absorption maximum λ_{max} and extinction coefficient ε of the different DAE isomers in solution are shown in Table S1.

While the solution-state results provide useful insights into these systems, solid state measurements are more applicable to materials applications.[5] Mirroring the solution-state experiments, kinetic tracking of the absorption maximum at 672 nm of PEO-*stat*-PAGE-DAE-X spin-coated thin films over time is shown in Figure 3 and Figure S13, S14. The ring-open to ring-closed isomerization reaction of all the three PEO-*stat*-PAGE-DAE-X copolymers follow a first order dynamic equilibrium model (Equation 1), while the reverse visible light driven ring opening kinetics are well described

$$\frac{[Closed\ form]_t}{[Open\ form]_0} = 1 - \frac{k_{open} + k_{close} * Exp[-(k_{open} + k_{close}) * t]}{k_{open} + k_{close}} \qquad (1)$$

by a first order decay.[31,32] It is noted that with UV light irradiation, k_{open} systematically decreases from I^- to BF_4^- to $TFSI^-$, while the k_{close} is only marginally impacted by the nature of the anion (Figure S14, Table S3). Additionally, the k_{open} with white light irradiation decrease on going from I^- to $TFSI^-$ is small (0.157 for I^- and 0.123 for $TFSI^-$). Using the λ_{max} and ε measured above, the conversion ratios of PEO-*stat*-PAGE-DAE-I, -BF_4, and -TFSI from ring-open to ring-closed isomer of solid films at the PSS

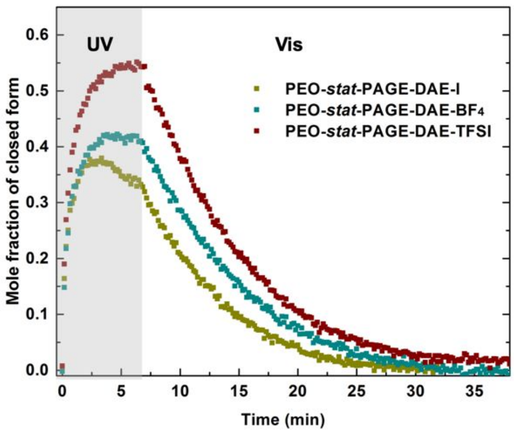


Figure 3. Pump probe measurements of PEO-*stat*-PAGE-DAE-X solid thin film with light irradiation. Light responsive amount changes of ring-closed isomers by tracking their absorption at 672 nm indicate the reversible photoswitch.

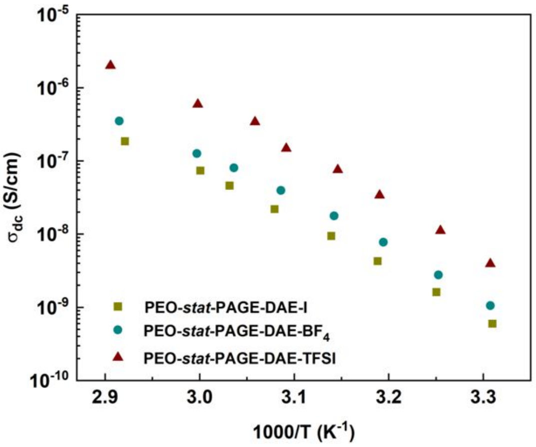


Figure 4. Ionic conductivity versus temperature for PEO-*stat*-PAGE-DAE-X polymers

with 300 nm light were found to be 37, 42, and 55% respectively. While these conversions are notably lower than those in the solution studies, we note that photoswitching in the solid state is highly dependent on a number of factors, including light penetration, and the free volume surrounding the tethered photoswitch. Despite the decrease in PSS, the TFSI$^-$ anion enables the largest conversion from ring-open isomer to ring-closed isomer, similar to solution studies. It is possible that the size of the counter anion may affect the extinction coefficients[33–35] which directly impacts the rate constants for the conversion between the open and closed states, and in turn leads to the variation of PSS. Work is ongoing to better understand the role the anion plays on modulating the PSS, as well as further strategies for modulating the PSS in the solid state.

The ionic conductivity of PEO-*stat*-PAGE-DAE-X copolymers with different anions was then probed using impedance spectroscopy to compare their ion transport, as shown in Figure 4 and S15. The conductivities of the corresponding PILs at room temperature (around 30 ^{o}C) and above room temperature are: TFSI$^-$ > BF$_4^-$ > I$^-$, presumably because of the gradually increased cation-anion interaction and decreased anion mobility with decreasing anion size. The calculated activation energy of these PILs are 1.17-1.34 eV by Arrhenius fitting, which is similar to other reported polymer electrolytes (Table S4).[36,37] Notably, the PIL with BF$_4^-$ anions exhibits the lowest activation energy from both Arrhenius and VFT fit, suggesting the relatively weak cation-anion interaction and small anion size both lead to lower potential energy barriers and less hindered free ion motion. For measurements of ionic conductivity change during light irradiation, in-plane conductivity analysis on spin-coated PEO-*stat*-PAGE-DAE-X PIL thin films was conducted on pre-cleaned quartz with evaporated Au electrodes for top contacts (Figure 5a, Figure S16). As shown in Figure 5b, the ionic conductivity of all PEO-*stat*-PAGE-DAE-X (I$^-$, BF$_4^-$ and TFSI$^-$) systems rapidly decreased 49, 33, and 46% respectively upon UV irradiation, and subsequently increased upon exposure to visible light. The light responsive ionic conductivity change was repeated over multiple cycles for each DAE-X derivative, with only a slight change in ionic conductivity being observed (Figure S17). It should be noted that the light sources used for pump probe measurements and light responsive ionic conductivity measurements are different, which leads to different irradiation times to reach PSS. However, only the PEO-*stat*-PAGE-DAE-BF$_4$ derivative fully switched back to its original conductivity value, while PEO-*stat*-PAGE-DAE-I and PEO-*stat*-PAGE-DAE-TFSI reversed back to 80% and 85% of their original performance (Figure 5b). Interestingly, with UV light irradiation, the PEO-*stat*-PAGE-DAE-I has the lowest ratio of ring-closed isomer (37%) but most pronounced light responsive ionic conductivity change (49%). Presumably this is due to a stronger cation-anion interaction that leads to a larger decrease in light induced conductivity. In addition, PEO-*stat*-PAGE-DAE-BF$_4$ features similar strength of cation-anion interaction, but around 13% lower ratio of ring-closed isomer under UV light irradiation than PEO-*stat*-PAGE-DAE-TFSI, resulting in a smaller ionic conductivity decrease. This result indicates that increasing the PSS also leads to a more pronounced change in light responsive ionic conductivity for the PILs. Here, for better comparison, a parameter, "Δσ(PSS)" of ionic conductivity was introduced, which is defined as the ratio of the maximum ionic conductivity decrease normalized by their PSS. This parameter represents the efficiency of ionic conductivity modulation with respect to PSS (Equation 2). As shown in Figure 5c, the Δσ(PSS) value of PEO-*stat*-PAGE-DAE-I is around 1.7 times higher than BF$_4$ and TFSI polymer films, while BF$_4$ and TFSI samples share similar values. This result clearly shows that PEO-*stat*-PAGE-DAE-I with the strongest cation-anion interaction leads to the most pronounced light responsive conductivity change.

$$\Delta\sigma(PSS) = \frac{maximum\ \sigma\ decrease}{PSS} \qquad (2)$$

From a fundamental perspective, the ability to change ionic conductivity with light irradiation in a single polymer system provides a unique handle for studying the underlying impact of ion-polymer interactions on ion transport. Key to this system is the non-invasive nature of the photo-modulation step which avoids the use of additional chemical species for modulating ionic conductivity. Previous studies on PIL ionic conductivity reveal that many factors such as cation-anion interaction, polymer T_g, and molar volume of counter ions all influence the ionic conductivity. In most cases, these factors are interdependent, and thus complicate mechanistic studies aimed at developing high conductivity PILs. In direct contrast, this novel system described above has the same anion and imidazolium containing DAE cations which are present in both the ring-open and ring-closed isomeric forms. Switching involves the formation and cleavage of a single C–C bond and therefore has minimal volume change. Taking PIL with BF_4^- anion as an example, DSC measurements show that the cation and anion interaction change on light irradiation has almost no influence on the T_g of PEO-*stat*-PAGE-DAE-BF_4 (open) and PEO-*stat*-PAGE-DAE-BF_4 (closed), with both systems showing values of 0 °C (Figure S17). As a result, the PIL based on PEO-*stat*-PAGE-DAE-BF_4 provides experimental evidence that stronger cation-anion interaction can lead to lower ionic conductivity without the competing effect of polymer T_g or anion volume changes. How this increased ion association affects ion aggregation and possible clustering behavior of the PIL requires further investigation. In addition, we will also explore the potential contribution from the electrochromism of the DAE based system.[38]

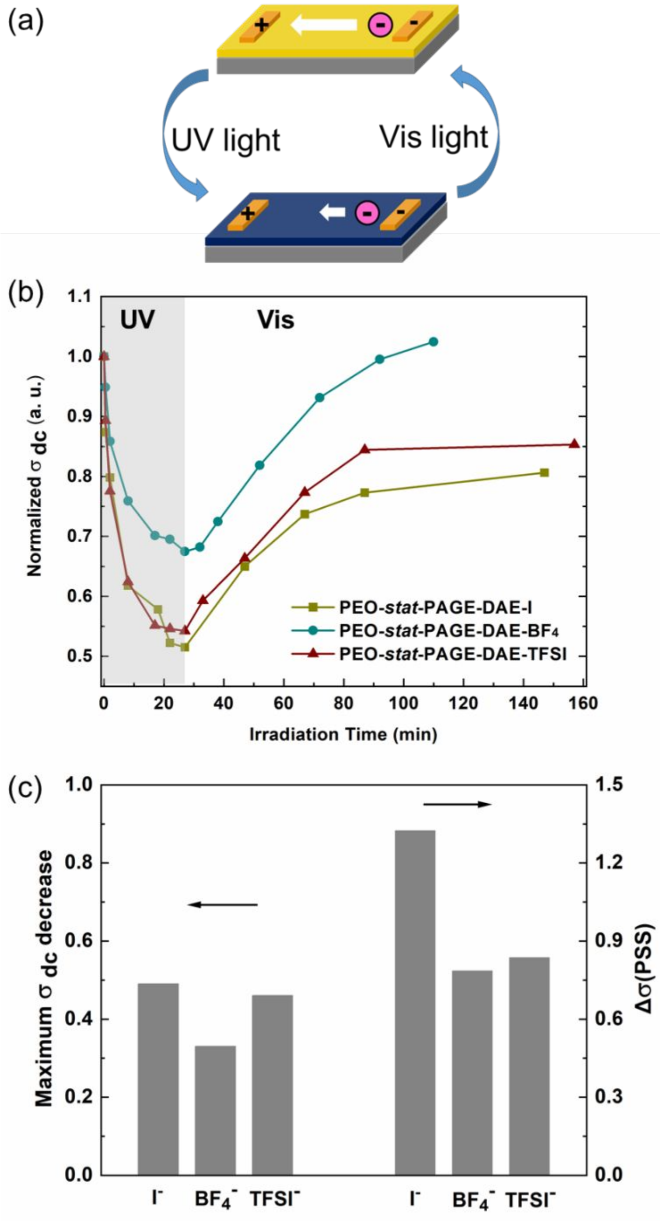


Figure 5. (a) Ionic conductivity measurement geometry and their light responsive properties. (b) Ionic conductivity changes of PEO-*stat*-PAGE-DAE-X (I, BF_4, TFSI) solid thin film with light irradiation. (c) Comparison of maximum ionic conductivity decrease and their maximum decrease normalized to PSS of PEO-*stat*-PAGE-DAE-X (I, BF_4, TFSI) solid thin film with UV light irradiation.

Conclusions

In conclusion, the incorporation of imidazolium containing DAE units as polymer side chains enable light responsive ionic conductivity. By varying the anion structure, the PIL with stronger cation-anion interaction and a higher PSS state leads to a more pronounced change in conductivity upon photoswitching from ring-open isomer to the ring-closed isomer, though with decreased reversibility. Based on these results, a promising direction in the development of high performance light responsive PILs is the synthesis of photoresponsive cations with stronger binding strengths with relatively "free" anions. In addition, this photoswitch containing PIL provides a versatile platform to study the influence of cation-anion interaction on ionic conductivity without competing effects of T_g and cation counterion size. Collectively, this work provides a path for future design and presents new opportunities in the field of light responsive PILs.

Conflicts of interest

The authors declare no competing financial interest.

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References

1 J. Czapinski, M. Kielbus, J. Kalafut, M. Kos, A. Stepulak and A. Rivero-Müller, *Front. Chem.*, 2017, **5**, 12.

2 F. P. Nicoletta, D. Cupelli, P. Formoso, G. de Filpo, V. Colella and A. Gugliuzza, *Membranes (Basel).*, 2012, **2**, 134–197.

3 G. Y. Kim, A. Senocrate, T. Y. Yang, G. Gregori, M. Grätzel and J. Maier, *Nat. Mater.*, 2018, **17**, 445–449.

4 H. Nie, J. L. Self, A. S. Kuenstler, R. C. Hayward and J. Read de Alaniz, *Adv. Opt. Mater.*, 2019, **7**, 1900224–1900245.

5 D. Mecerreyes, *Prog. Polym. Sci.*, 2011, **36**, 1629–1648.

6 G. E. Sanoja, N. S. Schauser, J. M. Bartels, C. M. Evans, M. E. Helgeson, R. Seshadri and R. A. Segalman, *Macromolecules*, 2018, **51**, 2017–2026.

7 N. S. Schauser, D. J. Grzetic, T. Tabassum, G. A. Kliegle, M. L. Le, E. M. Susca, S. Antoine, T. J. Keller, K. T. Delaney, S. Han, R. Seshadri, G. H. Fredrickson and R. A. Segalman, *J. Am. Chem. Soc.*, 2020, **142**, 7055-7065.

8 H. Wang, C. N. Zhu, H. Zeng, X. Ji, T. Xie, X. Yan, Z. L. Wu and F. Huang, *Adv. Mater.*, 2019, **31**, 1807328–1807335.

9 H. Nie, N. S. Schauser, N. D. Dolinski, J. Hu, C. J. Hawker, R. A. Segalman and J. Read de Alaniz, *Angew. Chem. Int. Ed.*, 2020, **59**, 5123–5128.

10 V. W. W. Yam, J. K. W. Lee, C. C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2009, **131**, 912–913.

11 R. Sumitani and T. Mochida, *Macromolecules*, 2020, **53**, 6968–6974.

12 U. H. Choi, Y. Ye, D. Salas De La Cruz, W. Liu, K. I. Winey, Y. A. Elabd, J. Runt and R. H. Colby, *Macromolecules*, 2014, **47**, 777–790.

13 C. Iacob, A. Matsumoto, M. Brennan, H. Liu, S. J. Paddison, O. Urakawa, T. Inoue, J. Sangoro and J. Runt, *ACS Macro Lett.*, 2017, **6**, 941–946.

14 O. Azzaroni, A. A. Brown and W. T. S. Huck, *Adv. Mater.*, 2007, **19**, 151–154.

15 N. S. Schauser, G. E. Sanoja, J. M. Bartels, S. K. Jain, J. G. Hu, S. Han, L. M. Walker, M. E. Helgeson, R. Seshadri and R. A. Segalman, *Chem. Mater.*, 2018, **30**, 5759–5769.

16 B. M. Neilson and C. W. Bielawski, *J. Am. Chem. Soc.*, 2012, **134**, 12693–12699.

17 M. Yoshizawa and H. Ohno, *Electrochim. Acta*, 2001, **46**, 1723–1728.

18 Y. Ye and Y. A. Elabd, *Polymer (Guildf).*, 2011, **52**, 1309–1317.

19 K. A. Perrine, K. M. Parry, A. C. Stern, M. H. C. Van Spyk, M. J. Makowski, J. A. Freites, B. Winter, D. J. Tobias and J. C. Hemminger, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 13363–13368.

20 S. Zhang, N. Sun, X. He, X. Lu and X. Zhang, *J. Phys. Chem. Ref. Data*, 2006, **35**, 1475–1517.

21 A. M. Fernandes, M. A. A. Rocha, M. G. Freire, I. M. Marrucho, J. A. P. Coutinho and L. M. N. B. F. Santos, *J. Phys. Chem. B*, 2011, **115**, 4033–4041.

22 M. Chen, J. W. Dugger, X. Li, Y. Wang, R. Kumar, K. M. Meek, D. W. Uhrig, J. F. Browning, L. A. Madsen, T. E. Long and B. S. Lokitz, *J. Polym. Sci. Part A Polym. Chem.*, 2018, **56**, 1346–1357.

23 A. D. Headley and N. M. Jackson, *J. Phys. Org. Chem.*, 2002, **15**, 52–55.

24 A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc. Dalt. Trans.*, 1994, **23**, 3405–3413.

25 P. Bonĥte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.

26 H. V. Huynh, T. T. Lam and H. T. T. Luong, *RSC Adv.*, 2018, **8**, 34960–34966.

27 G. Duan, N. Zhu and V. W. W. Yam, *Chem. - A Eur. J.*, 2010, **16**, 13199–13209.

28 M. Herder, B. M. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738–2747.

29 B. Oruganti, P. Pál Kalapos, V. Bhargav, G. London and B. Durbeej, *J. Am. Chem. Soc.*, 2020, **142**, 13941–13953.

30 D. Kitagawa, T. Nakahama, Y. Nakai and S. Kobatake, *J. Mater. Chem. C*, 2019, **7**, 2865–2870.

31 J. R. Hemmer, Z. A. Page, K. D. Clark, F. Stricker, N. D. Dolinski, C. J. Hawker and J. Read De Alaniz, *J. Am. Chem. Soc.*, 2018, **140**, 10425–10429.

32 M. S. Zayas, N. D. Dolinski, J. L. Self, A. Abdilla, C. J. Hawker, C. M. Bates and J. Read de Alaniz, *ChemPhotoChem*, 2019, **3**, 467–472.

33 J. N. Gayton, S. Autry, R. C. Fortenberry, N. I. Hammer and J. H. Delcamp, *Molecules*, 2018, **23**, 3051.

34 P. A. Bouit, C. Aronica, L. Toupet, B. Le Guennic, C. Andraud and O. Maury, *J. Am. Chem. Soc.*, 2010, **132**, 4328–4335.

35 A. C. Véron, H. Zhang, A. Linden, F. Nüesch, J. Heier, R. Hany and T. Geiger, *Org. Lett.*, 2014, **16**, 1044–1047.

36 Z. Li, Q. Yao, Q. Zhang, Y. Zhao, D. Gao, S. Li and S. Xu, *J. Mater. Chem. A*, 2018, **6**, 24848–24859.

37 D. Fauteux, *Solid State Ionics*, 1988, **28**–**30**, 923–928.

38 A. Peters and N. R. Branda, *J. Am. Chem. Soc.* 2003, **125**, 3404–3405.