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### Light-controllable Ionic Conductivity in a Polymeric Ionic Liquid

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Abstract: Polymeric ionic liquids (PILs) have attracted considerable attention as electrolytes with high stability and mechanical durability. Light responsive materials are enabling for a variety of future technologies due to their remote and noninvasive manipulation, spatiotemporal control and low environmental impact. To address this potential, responsive PIL materials based on diarylethene units have been designed to undergo light-mediated conductivity changes. Key to this modulation is tuning of the cationic character of the imidazolium bridging unit upon photoswitching. Irradiation of these materials with UV light triggers a ~70% drop in conductivity in the solid state that can be recovered upon subsequent irradiation with visible light. Significantly, this light responsive ionic conductivity enables spatiotemporal and reversible patterning of PIL films using light. This modulation of ionic conductivity allows for the development of light controlled electrical circuits and wearable photodetectors.

#### Introduction

lonic liquids, such as imidazolium salts, have generated significant interest as electrolytes across a wide range of disciplines due to their high ionic conductivity and minimal to no volatility.<sup>[1]</sup> The introduction of ionic liquid motifs along polymer backbones, forming polymeric ionic liquids (PILs), further enhances this utility with improved stability, mechanical durability and integration with other electronic components.<sup>[2,3]</sup> Light responsive materials have similarly attracted considerable attention in a wide range of applications based on their advantages of remote and noninvasive manipulation, inherent spatiotemporal control and minimization of the generation of additional waste.<sup>[4-6]</sup> Surprisingly, combining the advantageous features of both materials classes through the development of "smart" PILs with light controllable conductivity has lagged significantly behind other classes of electronic/ionic conducting materials.<sup>[7-12]</sup> Advances in tunable PILs would therefore enable cutting-edge applications based on photoconductive properties such as light-controlled electronic circuits<sup>[13-15]</sup> and wearable photodetectors.[16-18]

To enable the development of stimuli-responsive PILs, we sought to design an ionic liquid based photoswitchable motif that could be incorporated into a polymeric structure. While the incorporation

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of photo-responsive molecules in ionic liquid motifs has been previously reported,<sup>[19-24]</sup> incorporating these structures into PILs has yet to be demonstrated. The substantial challenge in identifying a light-controllable PIL centers on translating photonic energy into a property change that can control ion transport through a polymer matrix. Key considerations include straightforward synthesis, reversibility, operation in the solid state and rapid response time. We speculate that photochromic diarylethenes (DAEs) containing an imidazolium ring as the bridging unit will serve as an especially appealing target in this context. Photochromic DAEs can switch between ring open (DAE-O) and ring closed (DAE-C) isomers both in solution and solid state.<sup>[25-28]</sup> Moreover, the photoinduced rearrangement of the  $\pi$ bond in the bridging imidazolium ring can be used to control the electronic properties and chemistry of the imidazolium ring. Photochromic diarylethenes bearing an imidazolium ring have found applications in different areas such as photoswitchable organocatalysts,<sup>[29-31]</sup> chemical sensors,<sup>[32]</sup> and as a new type of Lewis acid.<sup>[33]</sup> For example, the Bielawski group used a DAEbased organocatalyst with photoswitchable electron density at the C2 position of the imidazole ring in N-heterocyclic carbene adducts to regulate the rate of transesterification reactions.[29] Additionally, Kawai showed that the open and closed isomers of 4,5-dithiazolylimidazolium derivatives possess different reactivity towards strong nucleophiles.[25]



**Figure 1.** (a) Photochromism of imidazolium bearing DAE; (b) Scheme of PIL with photoresponsive cation-anion interaction; (c) solid-state PIL film with tunable, photoresponsive ionic conductivity.

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Scheme 1. (a) Synthesis of primary amine functionalized DAE-BF4; (b) Synthesis of PIL PEO-*stat*-PAGE-DAE-BF4. Reagents and conditions: (i) N-3bromopropylphthalimide, cesium carbonate, DMF, 60 °C, 4 h; (ii) iodomethane, CH<sub>3</sub>CN, 80 °C, 16 h; (iii) hydrazine hydrate, 1,4-dioxane/H<sub>2</sub>O, reflux, overnight; (iv) silver tetrafluoroborate, THF/MeOH, room temperature, 15 min; (v) 3-Mercaptopropanyl-N-hydroxysuccinimide Ester, 2,2-dimethoxy-2-phenylacetophenone, DCM, 365 nm light, 0 °C, 2 h; (vi) DAE-BF4, triethylamine, DCM, room temperature, 36 h.

Here we describe the design of photoresponsive PILs using imidazolium containing DAEs as ionic pendants covalently attached to a poly(ethylene oxide) backbone. The ring-open isomer (DAE-O) contains a delocalized cationic change due to the aromatic imidazolium ring, while the ring-closed form (DAE-C) possesses more localized positive charge. This allows the binding between mobile anions and imidazolium containing DAE cations to be controlled, and thus the ionic conductivity of the PIL solid film reversibly modulated (**Figure 1**).

#### **Results and Discussion**

Previous work has demonstrated that photochromism in polymer systems is highly dependent on the  $T_g$  of the polymer matrix, where switching is favored in lower  $T_g$  polymers.<sup>[34]</sup> Here, a statistical copolymer of ethylene oxide and allyl glycidyl ether (PEO-stat-PAGE) (~10 mol% AGE) with a T<sub>g</sub> of around -60 °C was chosen as the PIL precursor.[35,36] First, a scalable and robust synthetic route was developed for DAEs bearing reactive primary amines for attachment to the polymer backbone. From the reported DAE 1, N-alkylation of the imidazole unit with N-3bromopropylphthalimide, followed by methylation with iodomethane afforded DAE 3. DAE-BF4 was produced by deprotection of the phthalimide group and subsequent anion metathesis. A N-hydroxysuccinimidyl (NHS) ester strategy was used to attach the DAE-BF4 to the PEO-stat-PAGE copolymer. The NHS ester group was first introduced onto PEO-stat-PAGE segments via thiol-ene click reaction, which can then selectively couple with DAE-BF4 under mild conditions to produce the desired DAE-containing PIL, PEO-stat-PAGE-DAE-BF4 (Scheme 1). A notable feature of this robust synthetic route is the ability to prepare gram quantities of DAE-containing PIL. The versatile synthetic route also enables control and modulation of backbone molecular weight, backbone identity and percent DAEincorporation, which are directions for future studies.

The electron density of the central imidazolium ring in DAE-BF<sub>4</sub> can be reversibly modulated using two different wavelengths of light. When DAE-BF<sub>4</sub> is present as the ring-open isomer (DAE-O), the imidazolium ring is conjugated with overlapping  $\pi$ -orbitals containing 4n+2  $\pi$  electrons. It is therefore expected to have significant aromatic character and delocalized positive charge. Irradiation with UV light triggers cyclization to give the ring-closed form with associated electronic rearrangement leading to a non-aromatic imidazolinium ring containing a more localized positive charge. Key to this strategy is the reversibility of this cyclization reaction which allows for regeneration of the aromatic ring-opened system upon irradiation with visible light.

Modulating the electron density of the imidazolium ring through light irradiation is expected to results in a stronger association of the BF4<sup>-</sup> anions with the closed DAE form than the open DAE form (Figure 2a). To demonstrate the aromaticity change and thus the ability to modulate electron density on the imidazolium unit and the anion interactions between the two photoisomers, initial studies examined changes in the <sup>1</sup>H NMR spectra for the DAE units in PEO-stat-PAGE-DAE-BF4 before and after photoswitching. Significantly, the C2 proton undergoes an upfield shift from 9.3 ppm to 8.9 ppm in CD<sub>2</sub>Cl<sub>2</sub> on UV light irradiation (Figure 2b and Figure S2). This shift is fully consistent with the

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corresponding small molecule analog where an upfield shift from 8.7 ppm to 8.2 ppm in CD<sub>3</sub>CN occurs on ring closure (**Figure S1**). Considering the imidazolium C2 proton sense a larger effective magnetic field in the aromatic ring-open isomer (DAE-O), an upfield shift is expected upon cyclization to the ring-closed isomer (DAE-O) despite the decrease in electron density of the ring-closed imidazolinium photoproduct. This decrease in electronic density upon photocyclization is supported by the <sup>13</sup>C NMR where the C2 carbon of the imidazolium shifts from 136.6 ppm to 150.6 ppm (**Figure S3**). A similar effect of decreasing the electron density and breaking aromaticity upon photocyclization has been reported by Kawai<sup>[25]</sup>, Bielawski<sup>[29]</sup> and Branda.<sup>[33]</sup>



**Figure 2.** (a) Illustration of cation-anion interaction change of PEO-*stat*-PAGE-DAE-BF<sub>4</sub> with light irradiation. (b) <sup>1</sup>H NMR overlay of photochromism of PEO-*stat*-PAGE-DAE-BF<sub>4</sub> (from open form to closed form) in CD<sub>2</sub>Cl<sub>2</sub> with UV light irradiation. (c) <sup>19</sup>F<sup>-1</sup>H CPMAS proton NMR spectrum of PEO-*stat*-PAGE-DAE-BF<sub>4</sub> in solid state at -18 °C under MAS at 25 kHz.

Additional solid-state NMR cross-polarization experiments before photoswitching revealed the ion carrier BF4<sup>-</sup> interacts strongly with the DAE cation units in PEO-stat-PAGE-DAE-BF4 rather than with other segments within the polymer. As shown in Figure 2c, proton peaks at 8.1 ppm (protons of a), 3.9 ppm (protons of b and b') and a shoulder around 2.4 ppm (protons of c) in the <sup>19</sup>F-<sup>1</sup>H cross polarization magic angle spinning (CPMAS) proton NMR spectrum were observed, revealing the BF4- cations are structurally close to the C2 position of the imidazolium ring.[37,38] Details of peak assignments and analysis of distance between BF4<sup>-</sup> and imidazolium cation before and after photoswitching from analysis of the corresponding CPMAS proton NMR spectra are shown in Figure S3, S4, S5 and Table S1. Here, analogous to similar small molecule photochromic systems,[25] it is deduced that the non-aromatic closed form (imidazolinium) has stronger interaction with the anion than aromatic open form (imidazolium) in our polymer system. However, we cannot rule out other factors that may affect anion mobility, such as reorientation of polymer chains and/or differential packing effects of the diarylethene units upon photocyclization.

To further characterize the photoswitching properties of PEO-stat-PAGE-DAE-BF4, a series of pump probe UV-Vis experiments were carried out and coupled with kinetic modeling to understand the impact of the surrounding environment on switching. For both the small molecule, DAE-BF<sub>4</sub>, and polymer supported system, PEO-stat-PAGE-DAE-BF4, irradiation with 300 nm light triggers photocyclization to generate the ring-closed isomer. This isomerization/switching reaction is characterized by a significant change in absorption profile which is visually observed through a colorless to blue transition and is due to the formation of extended π-conjugation in the ring-closed isomer. The corresponding UV-Vis absorption spectra show trends typically observed for ringclosing reactions of DAE derivatives. The high-energy bands (~300 nm), which are assigned to the n  $ightarrow \pi$  \* and  $\pi 
ightarrow \pi$  \* transitions of the N-heterocycle and thiophene systems, become less intense as broad bands centered at ~ 390 nm and 670 nm appear (Figure S6, S8).<sup>[26,29]</sup> By tracking this change in peak intensity (~300 nm and ~670 nm) the equilibrium ratio of the closed form can be estimated (full details can be found in the Supporting Information, Table S2, Table S3) and then fit with kinetic models. Significantly, the UV triggered isomerization reaction is well described by a first order dynamic equilibrium model (Equation 1) that has been previously used to characterize equilibrium processes for a variety of photochromic molecules. Additionally, the kinetics of the reverse visible-light-driven ring opening reaction are well described by a first order decay.<sup>[39,40]</sup>

$$\frac{[Closed form]_{t}}{[Open form]_{0}} = 1 - \frac{k_{open+k_{close}} * Exp[-(k_{open+k_{close}}) * t]}{k_{open+k_{close}}}$$
(1)

As expected, the equilibrium amount of closed form for the small molecule, DAE-BF<sub>4</sub>, increases as the solvent is changed from DCM (~45%), to THF (~65%), and MeCN (~70%), respectively. This change in isomer percentage with solvent polarity clearly

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illustrates the increased stabilization of the more localized positive charge for the closed form (**Figure S7**). This ring-closed isomer could also be reversibly switched to the open form with high efficiency by irradiating a solution of DAE-BF<sub>4</sub>-C with visible light. In contrast, this relationship between solvent polarity and isomer percentage is not observed for the polymer supported DAE derivative, PEO-*stat*-PAGE-DAE-BF<sub>4</sub>. For this material, all solvents equilibrate to roughly the same percentage of closed form DAE (~50%-55%) (**Figure S9**). It is proposed that the PEO-*stat*-PAGE polymer backbone provides a consistent molecular environment for the DAE side chains regardless of solvent, with the solvent polarity having only a minor effect on the photostationary states.



**Figure 3.** UV–Vis spectral changes of PEO-*stat*-PAGE-DAE-BF<sub>4</sub> solid film upon UV irradiation under ambient conditions. The photostationary state (PSS) is reached after UV irradiation for 22 min.

As applications for these novel PIL materials typically involves operation in the solid state, our focus was then directed to investigating the photochemical behavior of PEO-stat-PAGE-DAE-BF4 spin-coated thin films. Irradiation of PEO-stat-PAGE-DAE-BF<sub>4</sub> films with UV light again resulted in a distinct color change from near colorless to blue due to photoswitching of the DAE-BF4 units. In analogy with solution behavior, the UV-Vis spectra of PEO-stat-PAGE-DAE-BF4 films exhibited an absorption at ~300 nm (Figure 3, Figure S10) with rapid switching being observed upon UV irradiation leading to the appearance of new bands at 390 nm and 672 nm. Significantly, subsequent irradiation with visible light reversed these spectral changes, resulting in color loss. For photoswitching of the PIL thin films, kinetic tracking of the absorption maximum at 672 nm over time is shown in Figure S11 and Table S4. The above data clearly demonstrates the reversible photoswitching of polymersupported DAE-BF4 units in a solid film with isomerization ratio of ~ 38-44%. It should also be noted that under the same measurement conditions, the irradiation time required to reach the photostationary state is only marginally longer for both UV and Vis light irradiation when compared to solution, again consistent with

efficient photoswitching of the DAE units in a variety of environments.

The ability to photoswitch PEO-stat-PAGE-DAE-BF<sub>4</sub> PIL films then raises the exciting possibility of tuning ionic conductivity by controlling electron density of the imidazolium cation through reversible photocyclizations (Figure 4a). The bulk ionic conductivity of PEO-stat-PAGE-DAE-BF4 is 2 x 10-9 S/cm at room temperature with ionic conductivity increasing to 4.5 x 10<sup>-7</sup> S/cm upon addition of 50 wt% propylene carbonate (PC) as plasticizer (Figure S12).<sup>[41]</sup> Temperature-dependent ionic conductivity of PEO-stat-PAGE-DAE-BF4 follows Arrhenius-like behavior with a calculated activation energy of 1.07 eV, which is in a common range seen for other polymer electrolytes (Figure S13). For measurements of in-situ ionic conductivity change during light irradiation, through-plane analysis of spin-coated PEO-stat-PAGE-DAE-BF<sub>4</sub> PIL thin films on pre-cleaned ITO with evaporated Au electrodes for top contacts was conducted (Figure S14). Due to the decreased photoswiching efficiency with increasing temperature, all the ionic conductivity measurements were conducted at room temperature (Figure S15).



**Figure 4.** (a) Scheme illustrating the in situ conductivity measurement and ionic conductivity change of PEO-*stat*-PAGE-DAE-BF4 films with light irradiation. (b) lonic conductivity change of above solid films with light irradiation. (c) Open to

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closed form isomerization by monitoring UV-Vis absorption intensity at 672 nm of above solid films with light irradiation.

As shown in Figure 4b, the ionic conductivity of PEO-stat-PAGE-DAE-BF4 rapidly decreased by ~70% upon UV irradiation and subsequently could be switched back to its original value upon exposure to visible light. Compared with solution-based, light responsive ionic liquids, this new type of solid PIL material not only has the advantage of high ionic conductivity modulation but also simplified processing/operation for practical applications.<sup>[20-</sup> <sup>24]</sup> Significantly, the kinetics and time scale of ionic conductivity change parallels the change of isomerization of DAE-BF<sub>4</sub> units tracked by UV-Vis absorption spectroscopy, supporting that the photoswitch controls the property change (Figure 4c). This ionic conductivity change with light irradiation was reproducible for multiple cycles (Figure S16), albeit with a slight variation of ionic conductivity likely due to degradation of the DAE units as seen in UV-Vis studies.<sup>[42]</sup> DSC measurements show that the  $T_q$  of PEOstat-PAGE-DAE-BF4-O and PEO-stat-PAGE-DAE-BF4-C, stays the same (around 0 °C) (Figure S17). The static DP <sup>19</sup>F NMR spectrum becomes slightly broader when the DAE-BF4 units in the polymer are switched from an open to closed form with UV irradiation, also suggesting a tighter binding and thus reduction in the mobility of the BF4- anions. These observations are fully consistent with a decrease in ionic conductivity (Figure S18). The PEO-stat-PAGE-DAE-BF4 with PC sample shows similar light responsive ionic conductivity behavior as described above (Figure S19).

The unique light-responsive ionic conductivity property of PEOstat-PAGE-DAE-BF<sub>4</sub> PIL thin films now enables in-situ spatiotemporal patterning and reversible control over local conductivity. As a demonstration (Figure 5), PEO-stat-PAGE-DAE-BF4 thin films were patterned with Au electrodes (electrode 1 and 2). In state 1, the local ionic conductivity measured with electrode 1 and 2 is approximately identical. However, when the film is irradiated through a photomask with UV light, the DAE-BF4 units only undergo switching to their closed form under electrode 2. This results in a decrease in the local conductivity measured by electrode 2 while electrode 1 remains unchanged (state 2). UV light irradiation through the opposite photomask then leads to switching of the DAE units under electrode 1 and a similar decrease in ionic conductivity is observed (state 3). This patterning and modulation of local conductivity can be completely erased through Vis light irradiation, increasing the local conductivity of both electrodes (state 1). This ability to pattern ionic conductivity using simple masking and light exposure holds significant potential for novel stimuli-responsive electrical devices.



**Figure 5.** (a) Schematic illustration of light patterning ionic conductivity of PEOstat-PAGE-DAE-BF<sub>4</sub> with a through-plane configuration; (b) Local ionic conductivity with electrode 1 and 2 at different states.

#### Conclusion

In summary, we have developed a robust synthetic platform and demonstrated reversible photoswitching of DAE-based PILs. These PIL solid films feature continuously tunable ionic conductivity levels with irradiation time, and a notable maximum ~ 70% drop in conductivity. Taking advantage of this unique lightresponsive ionic conductivity property of PIL thin films, in-situ spatiotemporal patterning and reversible control over local conductivity was successfully illustrated. This new light responsive PEO-stat-PAGE-DAE-BF4 system is envisioned to lead to new opportunities and research directions for PIL materials, which hold great potential for smart electrical circuits and wearable photodetectors. Moreover, the non-invasive nature of the photomodulation step which avoids the use of any additional chemical species for modulating ionic conductivity provides a unique handle for future mechanistic studies. The design of imidazolium bearing photoswitches with improved fatigue resistance and thermal stability for next generation PILs and the impact of fundamental ion-polymer interactions on ion transport are under investigation.

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**Keywords:** diarylethene • polymeric ionic liquid • photoswitch • ionic conductivity • cation-anion interaction

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Light responsive polymeric ionic liquids: Responsive PIL materials based on diarylethene units have been designed to undergo a lightmediated change in conductivity. Key to this modulation is a change in the cationic character of the imidazolium bridging unit upon photoswitching. Irradiation of these materials with UV light triggers a ~70% drop in conductivity in the solid state that can be recovered upon subsequent irradiation with visible light.



higher ionic conductivity lower ionic conductivity

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Light-controllable Ionic Conductivity in a Polymeric Ionic Liquid