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Polymerizable Ionic Liquids for Fixed-Junction Polymer Light-Emitting Electrochemical Cells

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Light-emitting devices based on organic materials are promising candidates for new display and lighting technologies. Specifically, increasing interest is developing in polymer light-emitting electrochemical cells (LECs). In an LEC,[1−4] a blend of semiconducting polymer and electrolyte is sandwiched between a cathode and anode. Application of a suitable bias results in ionic dissociation and subsequent diffusion to the appropriate electrode. When the applied bias approaches the energy gap of the semiconducting polymer, electrochemical doping of the polymer can occur with the diffused ions serving as counter charges. The charge buildup and electrochemical doping processes reduce charge injection barriers and assist in the movement of charge carriers in the film, eliminating the need for low-work-function metals and allowing for more efficient charge injection and low turn-on voltages using Au or Al as the cathode metal. However, all steps of LEC operation are reversible, and removal of the external bias leads to device discharge followed by ion redistribution, resulting in unacceptably slow turn on times and disallowing their use as efficient photovoltaic devices.

Various approaches addressing the reversibility of the junction have been demonstrated. Physical immobilization of ions by freezing out ionic mobility,[5−7] modification of the glass-transition temperature of electroluminescent polymer,[8,9] and use of ionic liquids (ILs)[10−15] have been shown, among others. The latter was advantageous because of the ability of ILs to blend well with semiconducting and ion transport polymers. Approaches to retain the charge distribution employing chemical bond formation have also been demonstrated.[16−21] One such strategy employing covalent bond formation within a single-layer device has been previously demonstrated in our group.[17] In this study, [2-(methacryloyloxy)ethyl] trimethylammonium 2-(methacryloyloxy)ethane sulfonate (METMA/MES) was used as an ionic material in which both the cation and anion contained reactive α,β-unsaturated carbonyl functionalities that formed chemical bonds after ion distribution and electrochemical doping occurred. The resulting LECs showed unipolar light emission, diode-like rectification, and a linear relationship between current and radiance. However, phase incompatibility with semiconducting polymer resulted in poor performance.

Here, we describe the synthesis of novel ionic materials for use in an LEC device structure that combine the good processing properties of ionic liquids (such as good solubility in conventional organic solvents and good miscibility with emissive materials) with the ability of ion-pair monomers to form covalent bonds to achieve ion immobilization. The structures of the ionic liquids developed here are presented in Figure 1a. All three of these materials have a common anion, ally sulfonate, whereas the cation consists of trialkyl allyl (or vinyl)-substituted quaternary nitrogen. To affect processing properties, we varied the length of the alkyl chains attached to the quaternary nitrogen as follows: **ATOAAS**, C8; **ATBAAS**, C4; **TMVAAS**, C1. To enable bond formation, both the cations and anions of the three materials bear allylic/vinyllic functionalities. The materials were synthesized following the general procedure presented in Figure 1b. The appropriate trialkyl amine was quaternized with allyl bromide giving corresponding quarternary ammonium salts. Subsequent salt metathesis with silver allyl sulfonate afforded colorless to slightly yellow

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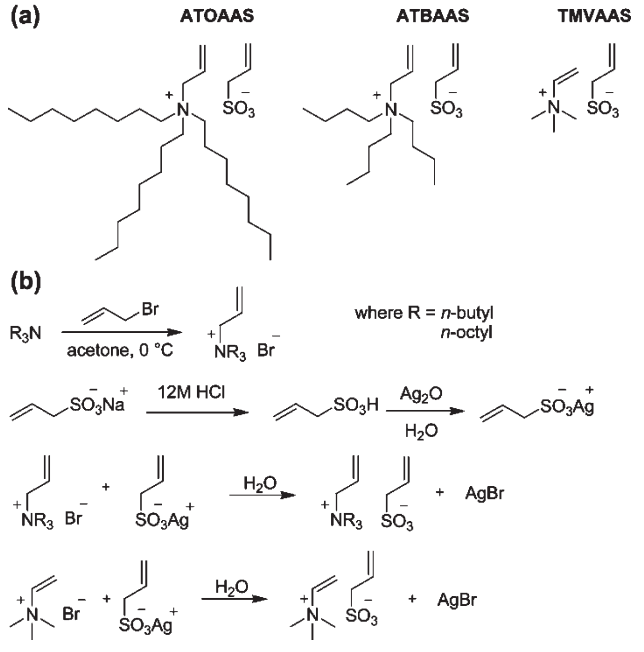

Figure 1. (a) Chemical structures of materials synthesized in this study. (b) General synthetic scheme. Further synthetic details for all materials can be found in Supporting Information.

waxy solids **ATOAAS** and **ATBAAS**. Compound **TMVAAS** (white crystalline solid) was synthesized starting from commercially available trimethylvinyl ammonium bromide following by the salt metathesis procedure described above. Materials **ATOAAS** and **ATBAAS** have melting points slightly below room temperature (15−20 °C), where as the melting point of **TMVAAS** was found to be 65−68 °C.

Devices were constructed using poly[2-methoxy-5-(3′,7′-dimethyl-octyloxy)-*p*-phenylenevinylene (MDMO-PPV) as the emissive polymer. A single-layer, sandwich-type architecture was used (Figure 2) in which the polymer solution (light-emitting polymer and polymerizable ionic liquid (PIL) in a 10:3.5 ratio at approximately 1% by total weight in chlorobenzene) was spin-cast onto patterned ITO glass substrates, followed by thermal evaporation of gold contacts. Because of the improved compatibility, solubility, and ease of ion dissociation in comparison METMA/MES, no PEO is required and there is minimal phase separation observed in these films (surface roughness of 1−2 nm was measured with AFM). This property is especially promising, as phase incompatibility between the emissive polymer and the typical electrolyte materials, irreversible overdoping of light-emitting polymer when mobile ions are employed, and accelerated film decomposition due to polyethylene oxide have been shown to result in poor performance and short lifetime of LECs.[4,12,13,17,22−30]

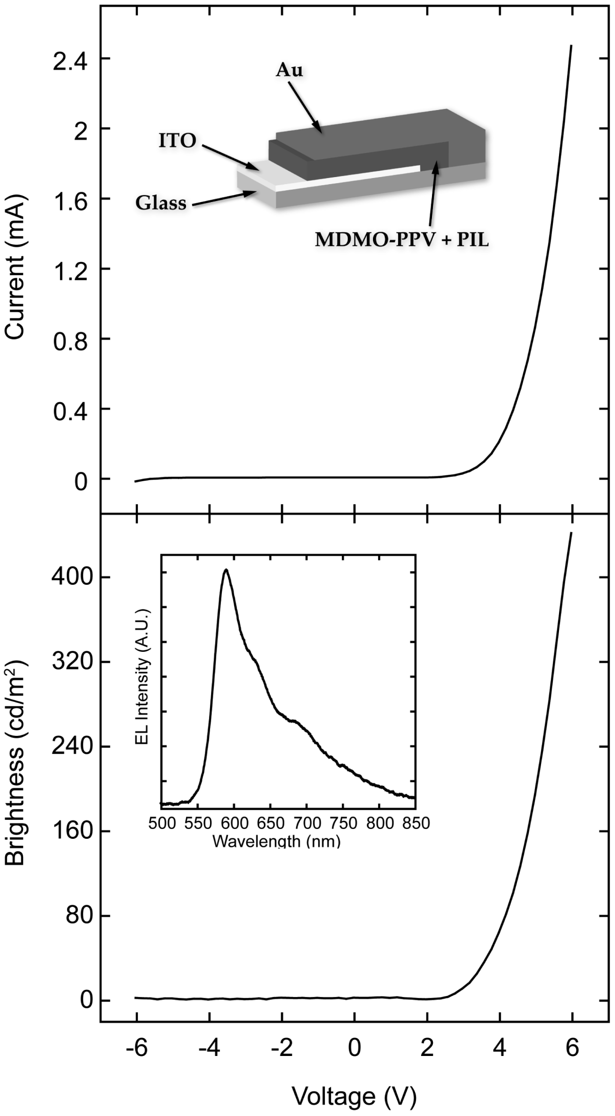

Figure 2. (a) Current and (b) brightness vs voltage curves for the light-emitting electrochemical devices using **ATOAAS** as the ionic material. Devices are charged at the maximum positive voltage as swept to negative voltage as described in the text. Insets show device structure and EL spectrum.

Devices are charged at 4−6 V (with ITO biased as the cathode) at room temperature in a nitrogen glovebox until a steady current is achieved, around 3−5 min. Voltage is then swept toward negative values in 0.2 V increments with a 100 ms delay between step and measure. Current−voltage and radiance−voltage measurements for a typical device are shown in figure 2. Devices emit uniform, red-orange light, and show an order of magnitude improvement in overall light emission and current over METMA/MES devices, with similar rectification ratios.[17] Overall, for devices using similar emissive materials, in terms of light output, operating voltage and rectification, these devices significantly outperform other reported fixed-junction LECs, and are similar in performance

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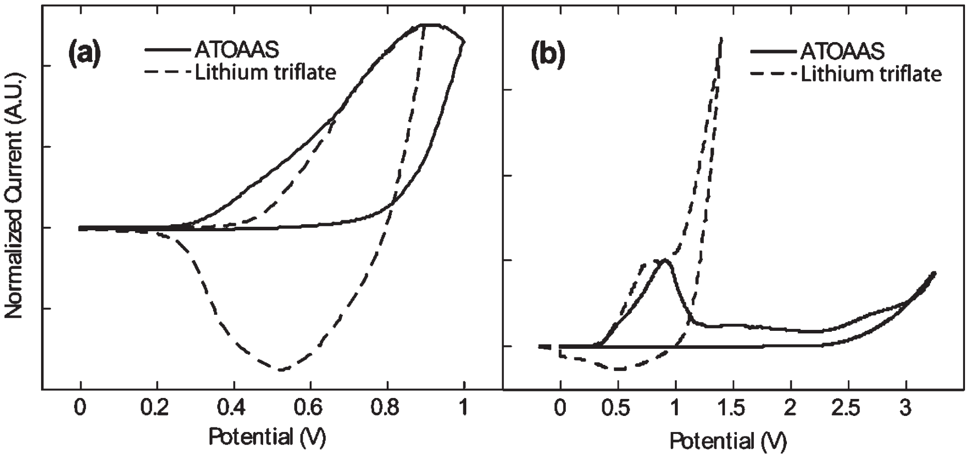

Figure 3. Cyclic voltammograms for the oxidation of MDMO-PPV films using 0.01 M lithium triflate or **ATOAAS** in acetonitrile as electrolyte. Scans are taken (a) to just past the first oxidation peak to demonstrate the difference in reversibility of oxidation and (b) to higher voltages to show the quenching of overoxidation when using the **ATOAAS** electrolyte. The onset of a second peak in the **ATOAAS** sample is present in scans of an ITO substrate blank.

to dynamic junction LECs using similar emissive materials, but demonstrating fixed-junction functionality.

The improvement in light output and current over devices made with METMA/MES can most likely be attributed to an improvement in film quality using these materials. However, device lifetimes were relatively short, depending on applied voltage (time to half brighness starting at 100 cd/m^2 was around 10 min). Because of the short lifetime, the devices were charged for a shorter time, resulting in a less-stable fixed junction under extended reversed bias operation. The reasons for the short lifetimes are unknown, but are consistent with observations of similar ionic liquid materials for which instabilities arise because of either the high loading of ionic liquid required for operation, or electrochemical instabilities in the ionic liquids themselves.[11,12,14] Nonetheless, the lifetimes of these devices are consistent with those of similar systems where reported. Strategies for addressing these issues via molecular design are the subject of ongoing work.

Devices were prepared from all three of the reported materials. The primary differences seen in the devices is related to the solubility and compatibility of the ionic material with the MDMO-PPV. The **ATOAAS** was the most soluble and resulted in films with very low observed phase separation as discussed above. The **ATBAAS** and **TMVAAS** showed progressively worse film morphology (with a roughness visible to the naked eye). The resulting changes to device performance were slower response and lower and less uniform overall light output.

Although the precise mechanism of bonding in these polymerizable counterion systems is not presently understood, one possibility is that a covalent bond is formed between the allylic/vynilic group and the emissive polymer that is initiated by the formation of a radical during electrochemical doping. This bond formation would then serve to prevent further doping as well as eliminating the reversibility of the doping reaction. The ability of **ATOAAS** to create a fixed junction was confirmed by examining the electrochemical doping process of MDMO-PPV using **ATOAAS** as the source of counterions. Electrochemistry experiments were performed using a nonaqueous silver/silver ion reference electrode (Ag/Ag$^+$, 0.3 V vs SCE), a platinum counter electrode, and a polymer film on ITO as a working electrode. The electrolyte consisted of 0.01 M lithium triflate or **ATOAAS** in acetonitrile. The loss of reversibility in the oxidation reaction of MDMO-PPV using **ATOAAS** in comparison with lithium triflate is seen in the absence of a negative return current in Figure 3a and is consistent with results using the METMA/MES as described previously. In Figure 3b, one can see the presence of a second reaction at higher voltages in the lithium triflate scan that is associated with the overoxidation of MDMO-PPV. However, in the **ATOAAS** electrolyte, this second peak was completely eliminated, indicating the suppression of the overoxidation reaction, also consistent with observations of oxidation using METMA/MES electrolytes.[17]

In conclusion, we demonstrated the use of polymerizable ionic liquids for application to polymer light-emitting electrochemical cells. Devices employing PILs had uniform film morphologies and showed diode-like behavior. In addition, brightness and turn-on times were improved by an order of magnitude compared to the ion-pair monomer based devices reported earlier. Further studies for optimizing PIL structure to improve device lifetime and stability are currently underway. A method for creating high performance fixed junction LECs can lead to advances in low-cost and low power consumption solid-state lighting and photovoltaic devices. In addition, the materials developed here may have further utility for additional applications in which control over ionic mobility or electrochemical doping is critical.

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Supporting Information Available: Details for synthesis of **ATOAAS**, **ATBAAS**, and **TMVAAS**; electrochemistry; device fabrication; and testing (PDF). This material is available free of charge via the Internet http://pubs.acs.org.