

Supporting Information for

**Electro-optical phenomena based on ionic liquids in
an optofluidic waveguide**

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Synthesis and Characterization of room temperature ionic liquids

All the seven ILs based on 1,3-methylimidazolium were synthesized by metathesis reactions from Bromide (Br⁻) precursors and equimolar amounts of the sodium salt or silver salt. Seven 1,3-imidazolium ILs with different cation and anion structures, namely, 1-Ethyl-3-methylimidazolium trifluoromethylsulfonyl [Emim][Nf₂T], 1-butyl-3-methylimidazolium trifluoromethylsulfonyl [Bmim][Nf₂T], 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄], 1-butyl-3-methylimidazolium perchlorate [Bmim][ClO₄], 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] and 1-ethyl-3-methylimidazolium dicyanamide [Emim][N(CN)₂], were synthesized in our laboratory according to the established procedures.

Prior to experiments, all of ILs were dried in vacuo at 80 °C for 3 hours. The water content was checked by Karl-Fisher analysis (Metrohm KF coulometer), and the water contents of those ILs are lower than 500 ppm. The bromide content was determined with a Mettler–Toledo Seven Multimetric with a bromide ion selective electrode, and the Br contents of all the ILs are lower than 0.1 wt.-%. The dynamic viscosity was measured on a Brookfield DV-III+ viscometer. For each IL, the ¹H NMR spectrum contains peaks corresponding to their cation and indicates no residual reactants. The characterization of ionic liquids was assessed by ¹H NMR spectra with a Bruker AMX-400 NMR spectrometer in [D₆] acetone solutions.

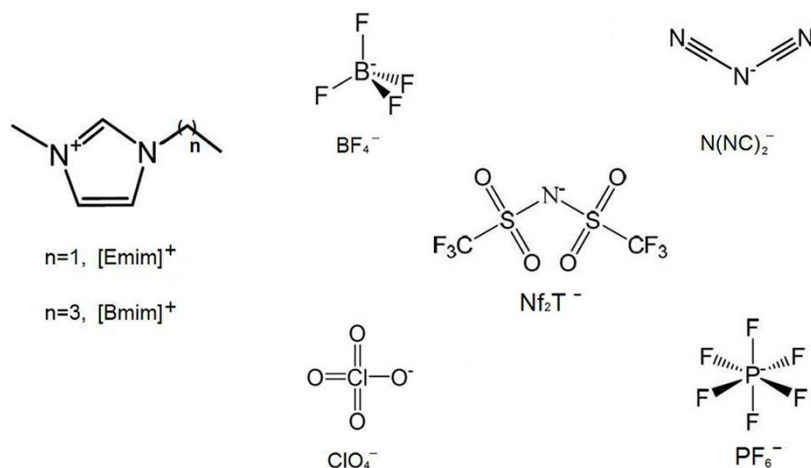


Fig. S.1. Formulas and structures of the ionic liquids used.

[Emim][Nf₂T]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=1.577(t, 3H), 4.069(s, 3H), 4.415(m, 2H), 7.713(s, 1H), 7.785(s, 1H), 9.032(s, 1H) ppm.

[Bmim][Nf₂T]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=0.9948(t, 3H), 1.388(m, 2H), 1.946(m, 2H), 4.075(s, 3H), 4.379(t, 2H), 7.730(s, 1H), 7.786(s, 1H), 9.046(s, 1H) ppm.

[Emim][BF₄]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=1.551(t, 3H), 4.028(s, 3H), 4.380(m, 2H), 7.686(s, 1H), 7.760(s, 1H), 8.975(s, 1H) ppm.

[Bmim][BF₄]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=0.944(t, 3H), 1.380(m, 2H), 1.919(m, 2H), 4.038(s, 3H), 4.350(t, 2H), 7.704(s, 1H), 7.759(s, 1H), 8.987(s, 1H) ppm.

[Bmim][ClO₄]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=0.945(t, 3H), 1.377(m, 2H), 1.928(m, 2H), 4.055(s, 3H), 4.362(t, 2H), 7.712(s, 1H), 7.769(s, 1H), 9.021(s, 1H) ppm.

[Bmim][PF₆]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=0.947(t, 3H), 1.387(m, 2H), 1.929(m, 2H), 4.050(s, 3H), 4.358(t, 2H), 7.693(s, 1H), 7.748(s, 1H), 8.956(s, 1H) ppm.

[Emim][N(CN)₂]: ¹H NMR(400 MHz, [D₆]acetone, 25 °C): δ=1.423(t, 3H), 3.839 (s, 3H), 4.192 (m, 2H), 7.668 (s, 1H), 7.763 (s, 1H), 9.089(s, 1H) ppm.

2. Fabrication of optofluidic chip

PDMS microfluidic channel

We fabricated the top sealing PDMS layer through standard soft lithography. The design of the chip was created by an AutoCAD program. We printed the photo-masks on transparent films and made the mold through photolithography. For the formation of the microchannel structures of the top layers, a 125μm-thick uniform film of negative photoresist SU-8 was coated on a silicon wafer by controlling the spin rate firstly. Then, after soft baking, the photoresist film was then exposed to UV light (wavelength 365 nm) with a photomask to form the microchannel structures. After the SU-8 master molds were fabricated, a 10:1 mixture of PDMS prepolymer and curing agent was cast over the master with a frame for holding the solution and cured for 1 h at 65 °C. The inverse structures of the SU-8 master mold were then transferred into the PDMS microchannels after the de-molding process.

Microelectrodes fabrication

The microelectrodes produced using photolithography, physical sputtering and lift-off of photoresist. A 4 inches glass disc was used as substrate. Firstly, the glass slides was cleaned with detergent, washed thoroughly with DI water and placed in an oven at 110 °C to dehydrate the surface for 20 mins. Then, about 10 μm thin photoresist was spin-coated on the substrate and baked at 125 °C for 1 minute on a hotplate. Photolithography patterning has been done with the UV light for 20 seconds through a transparency mask pattern. After development for about 1 min, we rinsed the slide with DI water and dried it with pure nitrogen. Then, A thin layer of 50 nm titanium layer acting as adhesion layer was sputtered on the slide, followed by a 100 nm thick platinum layer. In the following ion etch process; we removed the photoresist layer by soaking the slides in acetone with the aid of sonication for 10 min. Finally, we bonded PDMS microfluidic channels and glass slide with pattern electrodes together by plasma.

3. Simulation and experiment results

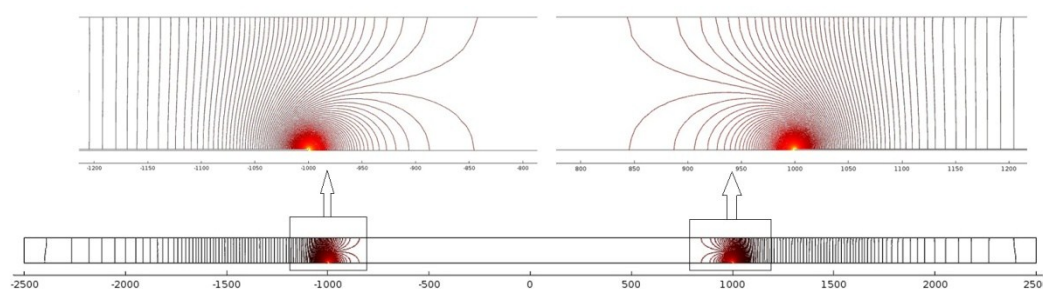


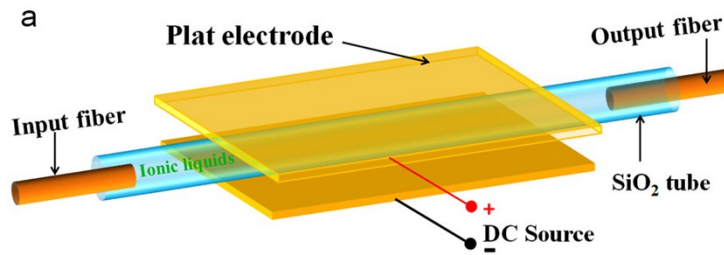
Fig. S.2. Simulated the distribution of electric field intensity long the waveguide for the first chip with commercial software COMSOL Multiphysics 4.3a. Under an applied voltage, the electric field intensity in the vicinity of the two electrodes terminal (about 1000 μm and -1000 μm) are much higher than other positions of the whole waveguide, due to the electrode is very thin. It should be noted that the sample is salt solutions in here. However, with an ionic liquid was applied, it will generates more larger electric fields in the vicinity of the electrode interface due to the ILs/electrode EDL structure.



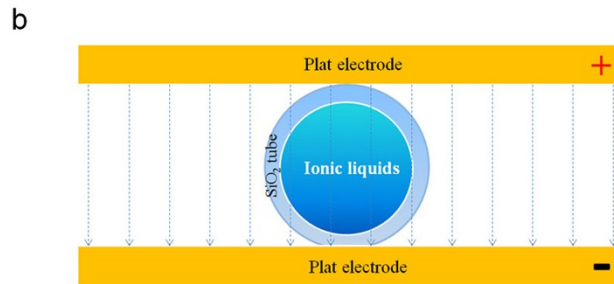
Fig. S.3. Experiment results of electro-optical modulation at 1530nm with and without a voltage applied for the ionic liquid [Emim][Nf₂T]. **a**, $U=0V$. **b**, $U=+3.5V$. **c**, $U=-3.5V$. The input fiber and output fiber was fixed at position A and B, respectively.

4. Electro-optical phenomena of ionic liquids under a strong external electric field

As is well known, ILs absorption characteristics are attributed to the imidazolium moiety and its various associated structures.¹ The anionic component plays a key role in the association of the cationic components (the imidazolium ions) and indirectly influences the optical properties of ILs. The previous molecular dynamics simulation study reveals that the structure of ILs could change from disordered to spatially homogeneous under an external electric field.² Therefore, the change of ~~change of~~ ILs structure (relative position between the anion and cation) could affect the optical properties of ionic liquids under a strong external electric field.



3D structure of the measure system



Cross section of the measurement system

Fig. S.4 The schematic of the experimental system for measuring electro-optical phenomena of ionic liquids under a strong external electric field. In our experiment, the lengths of the two plat electrodes are 8 cm, the length of SiO₂ tube is 10 cm. The input and output fibers were partly inserted into the tube.

The experimental system is shown schematically in Fig. S.4. Firstly, an ionic liquid sample was placed in a syringe, and promptly added to the SiO₂ tube (inner diameters: 300 μm, outer diameter: 500 μm) with very thin Teflon AF1600 coating ($n=1.29$) on internal surface. Light from laser source ($\lambda=663, 1330$ and 1530 nm) was coupled into the SiO₂ tube using an input Multimode optical fiber (cladding diameter: 125 μm, core diameter: 62.5 μm) with a numerical aperture of 0.22. The output fiber was connected with an optical spectrum analyzer to record the time-dependent optical peak powers under applied voltage. The two coupling fibers are partly inserted into the tube.

The distance of the two plat electrodes is 500 μm, it can generate a very strong static external electric field strength (about 200000 to 2000000 V/m) when a hundreds of volt voltage (100 to 1000 V) is applied. Under such a strong static electric field, the structure of ILs (the relative position of anions and cations) could change. Note that the electric field strength we used is lower than the electrical breakdown strength of air (about 3000000 V/m).

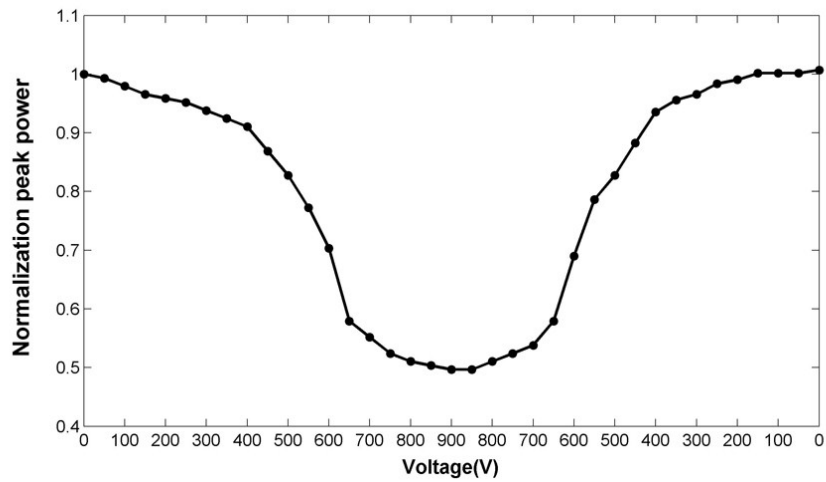


Fig. S.5 The electro-optical modulation of ionic liquid [Emim][Nf₂T] at 1530 nm as a function of the amplitude of the applied voltage. The voltage increases from 0 to 900 V, and then decrease from 900 to 0 V. The optical peak power was recorded after 9 seconds when a voltage was applied.

In **Fig. S.5**, we studied the normalized peak power as a function of applied voltage at a fixed wavelength of 1530 nm. With application of a voltage, the normalization peak power has a slightly decrease. It should be noted that the normalization peak power decreases quickly when the applied voltage at ranging from 400 to 650 V. With further increase of voltage, the normalization peak power decreases slowly and reaches to a constant value. With the decreasing of the applied voltage (from 900 to 0 V), the normalization peak power increase and return to the original values.

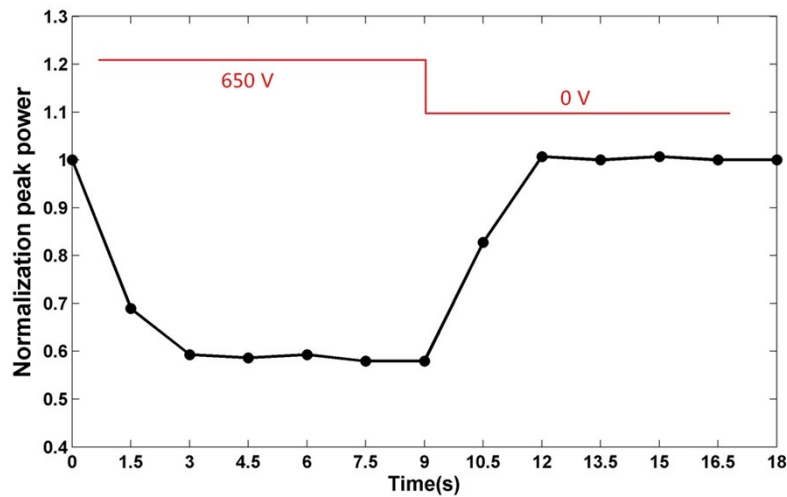


Fig. S.6 Temporal response of electro-optical modulation for ionic liquid [Emim][Nf₂T] at $\lambda=1530$ nm.

Temporal response of electro-optical modulation for ionic liquid [Emim][Nf₂T] at $\lambda=1530$ nm is shown in **Fig. S.6**. It should be noted that the electro-optical response time is about 3 seconds. However, the electro-optical response time in the lateral electric double-layer capacitor is tens of seconds. The large difference of the two electro-optical response speeds indicates that the modulation in the lateral EDL capacitor could mainly contributed by the change of carrier concentration(ions

redistribution near charged electrodes), the high ionic density of ILs cause the ions redistribution is kinetically slow, which induces the electro-optical response speeds is slow in the EDL capacitor.

In summer, under application of a very strong external electric field, the change of relative position between the anion and cation can contribute to the electro-optical modulation. However, the contribution of the change of ILs structure to the electro-optical modulation is very small when the external electric field is not very strong (less than 100000 V/m). Our result indicates that the modulation in the lateral electric double-layer capacitor is probably caused mainly by the change of carrier concentration.

References:

1. A. Paul and A. Samanta, Optical absorption and fluorescence studies on imidazolium ionic liquids comprising the bis (trifluoromethanesulphonyl) imide anion, 2006.
2. Y. Wang, *The Journal of Physical Chemistry B*, 2009, **113**, 11058-11060.