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Ionic liquid based variable focus lenses†

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This work presents ionic liquid based variable focus lenses using electrowetting, which exhibit excellent performance over a conventional saline based lens such as good tolerance of sharp temperature variation, wide operating temperature range (which is up to 100 °C) and in particular high stability at high temperatures.

Room temperature ionic liquids (RTILs or ILs) have emerged as a novel class of versatile solvent and soft material due to their negligible vapor pressure, wide liquid temperature range, intrinsic ionic conductivity and acceptable electrochemistry stability.[1] Besides these well-known properties, ILs could have good transparence in visible light, near-infrared and even in some other infrared regions, which renders them potential soft optic materials for multiple applications.[2] Recently, electrowetting of ILs has been studied and our previous results showed a reversible and wide contact angle modulation of ILs using oil as the medium and under an AC electric field, as compared to that in air or under a DC electric field.[3] In particular at a high frequency of 1 kHz, stable, sensitive, reversible and wide contact angle modulation (122–137°) was obtained.[4]

Electrowetting-based variable focus liquid lenses (EVFLL) have attracted considerable attention in mobile phones, barcode readers, medical equipment and various other optical systems.[5] Nevertheless, the most frequently used conductive liquid in EVFLL has been limited to saline. The traditional saline-based EVFLL could only work in a narrow temperature range (−20–60 °C), which may suffer from problems such as high focusing voltage, evaporating or freezing at relatively higher/lower temperatures, opacity in the near-infrared and even in most of the infrared range.[6] Therefore, development of liquid media with lower focusing voltage, wide temperature stability and wide light spectra ranges for EVFLL should be highly desirable. Herein, based on our previous efforts on IL electrowetting, we report the first IL-based EVFLL. The IL-based EVFLL can not only overcome the problems mentioned above but also work more efficiently than saline-based EVFLL, for example, it can focus under much lower voltages and work at higher temperatures.

Nine imidazolium ILs, *e.g.*, [EMIm][ClO_4], [BMIm][ClO_4], [BPy][BF_4], [EMIm][NTf_2], [EMIm][$N(CN)_2$], [BMIm][CF_3SO_3], [BMIm][NO_3], [EMIm][BF_4] and [BMIm][PF_6], with a wide refractive index distribution (1.4089–1.5329) were synthesized according to the literature[7] and adopted as conducting liquids owing to their good transparency in both visible light and near-infrared regions. All the ILs are transparent and colorless, with purity >99%, except for [EMIm][ClO_4] and [EMIm][$N(CN)_2$], whose purity is >97%. The surface tension, viscosity, and refractive index of all ILs were also measured (ESI,† Fig. S8, Fig. S9 and Table S1). Dodecane, previously identified as a suitable medium in three-phase electrowetting devices owing to its negligible solubility of ILs, low surface energy and low volatility, was chosen as the ambient insulating liquid. A typical IL-based EVFLL (Fig. 1), according to the typical fabrication of saline-based EVFLL reported by Kuiper *et al.*,[8] is composed of a cylindrical steel electrode (3–4 mm × Φ 2–4 mm) and ITO counter-electrode. The cylindrical steel electrode was covered with insulating and hydrophobic layers in which two immiscible liquids, *i.e.* 20 μL conducting IL (bottom) and insulating dodecane (upper) were filled to the full. Instead of DC, a 1 kHz AC power supply with 0–100 V was applied since a high frequency electric field facilitates stable and high efficiency electrowetting of ILs.[9] The experimental setup and detailed properties of ILs are available in ESI.† The focal length of a liquid lens is defined as the distance from the tangent point of the meniscus curvature to the focal points of the lens. For a concave lens, the focal length is the distance to the point from which a collimated beam appears to be diverging after passing through the lens (Fig. 2 (a)), and is negative ($f < 0$). For a convex lens, the focal length is the

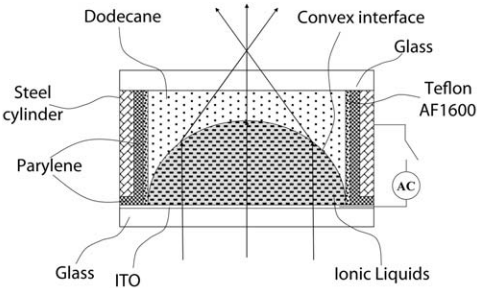

Fig. 1 Schematic cross section of an IL-based EVFLL.

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† Electronic supplementary information (ESI) available: Details of the synthesis, characterization, experiment device, physical measurements, equation derivation and other IL-based EVFLL experiment results. See DOI: 10.1039/c1sm05585b

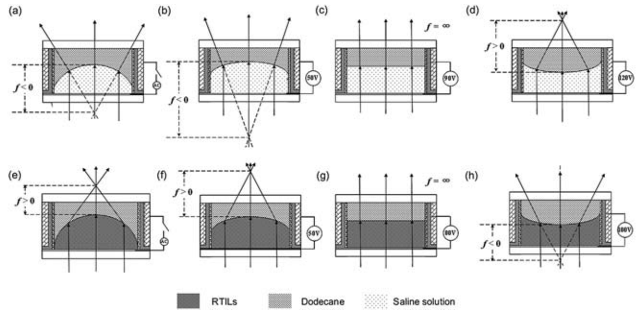

Fig. 2 The curvature of the meniscus of a saline-based EVFLL under 0, 50, 90, 120 V (a–d) and that of an IL-based EVFLL under 0, 50, 80, 100 V (e–h).

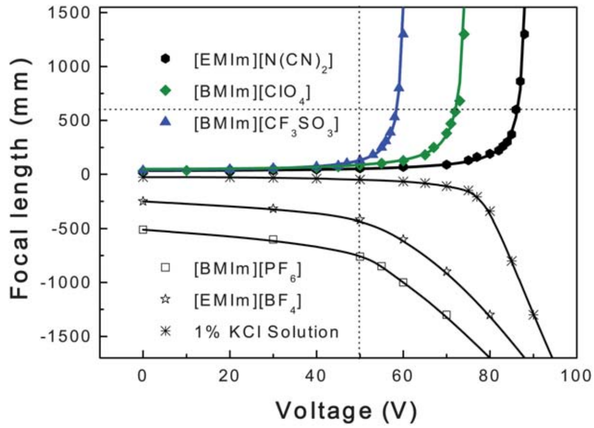

Fig. 3 Change of focal length of five typical ILs and saline-based EVFLL with applied voltage. The solid lines are theoretical curves.

distance at which a beam of collimated light will be focused to a single spot (Fig. 2 (e)), and is positive ($f > 0$). When the voltage is applied and increased across the two electrodes, the electric field changes the wettability of ILs and lowers the interfacial tension between ILs and the insulator (Parylene and Teflon AF1600) effectively,[10] thus the curvature of the meniscus changes. Depending on the curvature variation from convex to flat and even to concave, variable focus is achieved (Fig. 2). Higher curvature modulation would result in a larger focal length variation range. In this work, convex profile will be discussed principally.

Firstly, the relations between focal length and voltage within different ILs were tested (ESI,† Fig. S11). For most IL-based EVFLL, positive focal length ($f > 0$) was obtained with short initial focal length at zero voltage and large variable focus range. However, [EMIm][BF_4] and [BMIm][PF_6]-based EVFLL exhibit negative focal length ($f < 0$), similar to saline-based EVFLL. The different focusing behavior of IL-based EVFLL may be explained as follows: for conventional saline (or [EMIm][BF_4], [BMIm][PF_6])-based EVFLL, the lower refractive index ($\Delta n = n_{\text{saline}} - n_{\text{dodecane}} < 0$) and higher surface tension (($\Delta\sigma = \sigma_{\text{saline}} - \sigma_{\text{dodecane}} > 0$, convex profile) caused it to act as a concave lens at zero voltage (Fig. 2 (a)), which means focusing could only be achieved when the interface is forced from convex to concave by applying a higher voltage (>90 V, Fig. 2 (d)). However, unlike the case of saline-based EVFLL, for most IL-based EVFLL, both the higher refractive index ($\Delta n = n_{\text{IL}} - n_{\text{dodecane}} > 0$) and surface tension ($\Delta\sigma = \sigma_{\text{IL}} - \sigma_{\text{dodecane}} > 0$, convex profile) of ILs mean that they behave primarily as a convex lens below 80 V (Fig. 2 (e)–(f)) and focusing could be achieved under profile (<80 V). Thus, the focusing voltage of IL-based EVFLL is lower than that of saline-based EVFLL.

The typical results (Fig. 3) showed that the applied voltage (V) to obtain the same f 600 mm (horizontal dashed line in Fig. 3) give $V_{\text{BMImCF3SO3}}$ (53 V) < V_{BMImClO4} (72 V) < $V_{\text{EMImN(CN)2}}$ (86 V), and $f_{\text{BMImCF3SO3}}$ (130 mm) > f_{BMImClO4} (85 mm) > $f_{\text{EMImN(CN)2}}$ (55 mm) when the applied voltage (V) was set at 50 V (vertical dashed line in Fig. 3). In order to explain these phenomena, a simple model was developed.[11] According to this theory, the focal length for a given IL-based EVFLL, f, could be written as (see ESI† for the derivation)

$$f = \frac{1}{\left(\frac{n_{\text{dodecane}} - n_{\text{IL}}}{r}\right)\left(\cos\theta_0 + \frac{\varepsilon_0\varepsilon_r}{2d\sigma_{\text{IL-dodecane}}}V^2\right)} \quad (1)$$

As expected, the theoretical value is close to the experimental result (ESI,† Fig. S7). According to eqn (1), for a given IL-based EVFLL, where n_{dodecane}, r, ε_r and d remain constant, considering θ_0 is a function of $\sigma_{\text{IL-dodecane}}$ and $\sigma_{\text{IL-dodecane}}$ is directly proportional to σ_{IL}, f depends only on n_{IL}, σ_{IL}, and V. It can be represented as,

$$f = (n_{\text{IL}}, \sigma_{\text{IL}}, V) \quad (2)$$

It could be easily obtained that the focal length (f) of IL-based EVFLL depends on both the refractive index (n_{IL}) and the surface tension (σ_{IL}) of the IL under each separate voltage (V) in accordance with eqn (1) and (2). Furthermore, low refractive index (n_{IL}) and low surface tension (σ_{IL}) guarantee large focal length (f) under the same voltage (V). Moreover, the decreasing of refractive index (n_{IL}) and surface tension (σ_{IL}) leads to applied voltage (V) decreasing for identical focal length (f). Considering $n_{\text{BMImCF3SO3}}$ (1.4361) < n_{BMImClO4} (1.4709) < $n_{\text{EMImN(CN)2}}$ (1.5329) and $\sigma_{\text{BMImCF3SO3}}$ (31.736 mN m^{-1}) < σ_{BMImClO4} (38.305 mN m^{-1}) < $\sigma_{\text{EMImN(CN)2}}$ (45.924 mN m^{-1}), there are $V_{\text{BMImCF3SO3}} < V_{\text{BMImClO4}} < V_{\text{EMImN(CN)2}}$ to reach the same focal length (f) and $f_{\text{BMImCF3SO3}} > f_{\text{BMImClO4}} > f_{\text{EMImN(CN)2}}$ when applied voltage (V) is kept constant. This is in good conformity with the experimental results in Fig. 3.

The performance of IL-based EVFLL at high temperature was further investigated (ESI,† Fig. S12). As expected, IL-based EVFLL could work well at high temperatures with high efficiency apart from [EMIm][$N(CN)_2$]. Its color changes at high temperatures, which means that [$N(CN)_2$]-based ILs can not be used at temperatures >60 °C. Take an [EMIm][ClO_4]-based EVFLL for example (Fig. 4): with increasing temperature, the initial focal length (f_0) at zero voltage is slightly increased while the driving voltage (V) of the lens to obtain an identical focal length (f) is obviously decreased. This is probably due to the temperature-induced obvious decrease of surface tension (σ_{IL}).[12] Low surface tension (σ_{IL}) guarantees small interface tension ($\sigma_{\text{IL-dodecane}}$), which results in the decrease of driving voltage (V) to obtain an identical focal length (f) according to eqn (1). Thus, increasing temperature reduces the driving voltage (V) of the lens. Compared with traditional saline-based EVFLL, IL-based EVFLL worked even better at high temperature with not only high efficiency but also fast response. We believe that the response time (T) of IL-based EVFLL is influenced by the viscosity (δ) of the IL. In order to prove the conjecture, the response times of five IL-based EVFLL were investigated. It was found that $T_{\text{BMImNO3}} > T_{\text{BPyBF4}} > T_{\text{BMImCF3SO3}} > T_{\text{EMImN(CN)2}} > T_{\text{EMImNTf2}}$ (Fig. 5 left). Considering

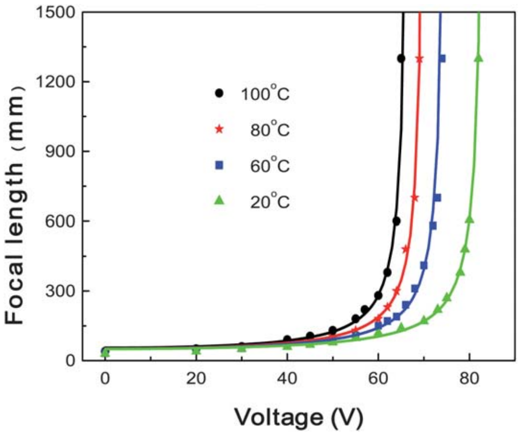

Fig. 4 Change of focal length of $EMImClO_4$-based EVFLL with applied voltage at variable temperature. The solid lines are theoretical curves.

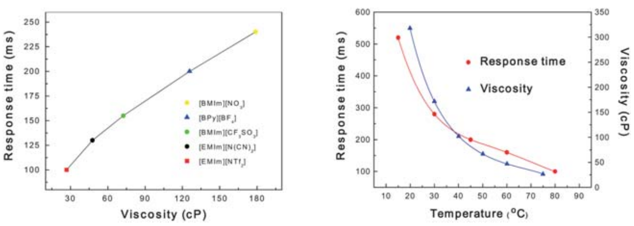

Fig. 5 Response times of five IL-based EVFLL with different viscosities (left) and $[EMIm][ClO_4]$-based EVFLL at variable temperature (right).

$\delta_{BMImNO3} > \delta_{BPyBF4} > \delta_{BMImCF3SO3} > \delta_{EMImN(CN)2} > \delta_{EMImNTf2}$, it could be concluded that low viscosity (δ) leads to short response time (T). As shown in Fig. 5 (right), the response time of $[EMIm][ClO_4]$-based EVFLL obviously decreases from 530 ms at 15 °C to 100 ms at 80 °C. Such a decrease in the response time curve (●) is suggested to originate from the significant temperature-induced diminution of viscosity (▲). Hence, our experiment results demonstrate that ILs with low viscosity could be better choices for shortening the response times of IL-based EVFLL.

Although the use of AC voltage usually implies more important losses, AC voltage was still used instead of DC because of good reversibility, wide contact angle modulation of ILs and avoiding residual charging effects under AC electric field, as compared to that under DC electric field. The power consumption of IL-based EVFLL slightly increases with increasing temperature and amount of IL; however, the average value (*ca.* 0.2 mW) is much lower than that for the traditional saline-based EVFLL (*ca.* 1 mW)[13] (ESI,† Fig. S13–S15). Furthermore, after hundreds of times switching or exposing the lens at about 80 °C for several days, the IL-based EVFLL can be also performed well without obvious corruption.

Another advantage for IL-based EVFLL which should be noted is the good transmittance in both visible light and near-infrared regions (400–1100 nm). The intensive absorption around 900 nm by saline limited the imaging performance of saline-based EVFLL in the near-infrared region. However, ILs shows a good transmittance between 400 and 1100 nm (ESI,† Fig. S10). Thus the IL-based EVFLL could have potential applications in near-infrared image systems since most ILs are optically transparent in this region.

In conclusion, the IL-based EVFLL exhibits excellent performance over saline such as wide operating temperature, tunable focus behavior, low energy consumption and in particular high stability at high temperatures. Besides, the performance of IL-based EVFLL affected by the physicochemical properties of ILs such as refractive index, surface tension, *etc.*, can be further improved through rational design and synthesis of ILs. These IL-based EVFLL could show potential applications in optics where robustness, size, working temperature, infrared transmittance and power consumption are critical.

Acknowledgements

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