## Anisotropic Ionic Conductivity in Fluorinated Ionic Liquid Crystals Suitable for Optoelectronic Applications

Antonio Abate<sup>1,2</sup>\*, Annamaria Petrozza<sup>3</sup>, Gabriella Cavallo<sup>1,3</sup>, Guglielmo Lanzani<sup>3,4</sup>, Francesco Matteucci<sup>5</sup>, Duncan W. Bruce<sup>6</sup>, Nikolay Houbenov<sup>7</sup>, Pierangelo Metrangolo<sup>1,3</sup>\* and Giuseppe Resnati<sup>1,3</sup>\*

 <sup>1</sup>NFMLab – D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milano, Italy
<sup>2</sup>Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU, United Kingdom
<sup>3</sup>Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy
<sup>4</sup>Dipartimento di Fisica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy
<sup>5</sup>TRE Tozzi Renewable Energy SpA, I-48010 Mezzano, RA, Italy
<sup>6</sup>Department of Chemistry, University of York, Heslington, YORK YO10 5DD, UK
<sup>7</sup>Molecular Materials, Department of Applied Physics, Aalto University, School of Science, P.O. Box 15100, FI-02015 Espoo, Finland

[\*] Corresponding authors: Tel.: +441865272354 (A.A.), +390223993041 (P.M.), 3032
(G.R.); Fax: +390223993180.

*E-mail addresses:* <u>a.abate1@physics.ox.ac.uk</u>, <u>pierangelo.metrangolo@polimi.it</u>, <u>giuseppe.resnati@polimi.it</u>.

## **Supplementary Information**



**Figure S1**. Differential scanning calorimetry trace of  $R_{H1}ImC_2R_{F6}$  showing that FILCs have a strong tendency to supercool on cooling. The same trend was observed for the other FILCs by heating-stage polarising optical microscopy.



**Figure S2**: Photocurrent-voltage curve for a DSSC employing  $R_{H8}ImC_3R_{F6}$  as electrolyte, under standard illumination conditions (AM 1.5, 100 mW cm<sup>-2</sup>). In the table below the figure, the device merit parameters: open circuit voltage (V<sub>oc</sub>), short circuit current (J<sub>sc</sub>), fill factor (FF) and efficiency ( $\eta$ ).

*Dye sensitized solar cell preparation:* Prepared DSSCs consist of a conducting glass substrate (F-doped SnO<sub>2</sub>) that was covered with a dense 500 nm TiO<sub>2</sub> layer, deposited by spray pyrolysis. On top of this layer, a nanoporous TiO<sub>2</sub> film was produced by doctorblading a paste containing 50 nm anatase particles. After subsequent annealing to 250 °C a second layer of scattering TiO<sub>2</sub> film was formed containing 350/450 nm anatase particles. The resulting photoelectrodes of 15 µm thickness, were gradually heated up to 450 °C in air and subsequently sintered at that temperature for 10 min. The substrates were immersed in 0.04 M TiCl<sub>4</sub> solution for 30 min at 70 °C followed by calcination at 450 °C for 30 min. When the temperature decreased to 40 °C, the electrodes were immersed into a diterabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) dye solution (0.4 mM in acetonitrile and *tert*-butanol in volume ratio 1:1) for 16 hours. After the soaking of the dye solution, the electrodes were rinsed in acetonitrile. The devices were assembled with thermally platinized TCO as counter electrode, using a thermoplastic frame (Surlyn 25 µm thick). The prepared FILC electrolyte

with iodine (0.25 eq), guanidinium thiocyanate (0.15 eq.) and *tert*-butylpiridine (0.8 eq.), was infiltrated by heating the prepared mixture at 70 °C.



Figure S3: <sup>1</sup>H NMR spectrum of R<sub>H8</sub>ImC<sub>3</sub>R<sub>F6</sub>.



**Figure S4**: <sup>19</sup>F NMR spectrum of  $R_{H8}ImC_3R_{F6}$ .