Liquid Crystalline Ferroelectronics in Supramolecular Nanostructures

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In contrast to conventional solid-state electronic materials, we have paid attention to soft matter with optoelectronic functions constructing a new research field of *Soft Matter Electronics*.[1,2] In nanostructures of liquid crystals and polymers, physical and chemical processes couple mutually to create new functional materials. We are studying 'Liquid Crystalline Ferroelectronics' based on coupling of the electronic charge carrier transport and ferroelectricity in nanostructured liquid crystal phases consisting of chiral molecules with extended π-conjugated units.[3]

We synthesized π-conjugated liquid crystals **1** and **2** consisting of a terthiophene unit and chiral side chains, exhibiting ferroelectricity and photoconductivity (Figure 1(a)). In the ferroelectric phase, we first observed a bulk photovoltaic effect driven by the spontaneous polarization. The polarity can be reversed by the polarity inversion of the poling treatment.[4,5] The polarized state can be immobilized in the ordered phase to enhance the photovoltaic effect.[6] In the ferroelectric phase of compound **2** mixed with a fullerene derivative, the external quantum efficiency in NUV-blue light region exceeded 75 % and the open circuit voltage reached 1.2 V in spite of the symmetrical device structure (Figure 1(b)).[7]

Electroluminescence is also observed in the ferroelectric phase of compound **2**, due to the reduced carrier injection barriers by the internal electric field. The efficient light emission is possible in thick samples and chemically unstable cathodes are not required. From a uniaxially aligned sample, linearly polarized light is obtained, and the polarized plane can be rotated in 90 degrees by the inversion of the DC bias polarity in the polling treatment (Figure 1(c)).[8]

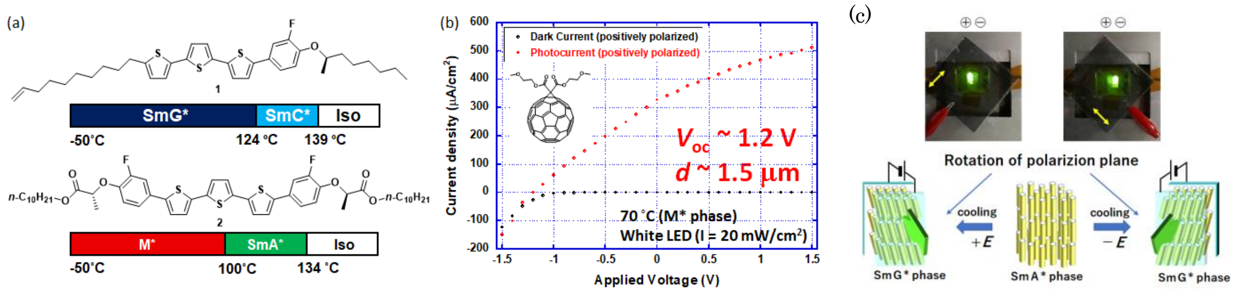

Figure 1 (a) Molecular structures of π-conjugated liquid crystals **1** and **2**. (b) J-V characteristics of the bulk photovoltaic effect in compounds **1** and **2** (c) Linearly polarized OLEDs using compound **2** and rotation of the polarized plane.

Recent publications related to this topic

1. T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno, M. Funahashi, "Transport of ions and electrons in nanostructured liquid crystals", *Nature Reviews Materials*, **2**, 17001 (2017).
2. M. Funahashi, "Nanostructured Liquid-Crystalline Semiconductors - A New Approach to Soft Matter Electronics", *J. Mater. Chem. C*, **2**, 7451-7459 (2014).
3. M. Funahashi, "Solution-processable electronic and redox-active liquid crystals based on the design of side chains", *Flex. Print. Electron*., 5, 043001 (2020).
4. Y. Funatsu, A. Sonoda, M. Funahashi, "Ferroelectric liquid-crystalline semiconductors based on a phenylterthiophene skeleton: Effect of introduction of oligosiloxane moieties and photovoltaic effect", *J. Mater. Chem. C*, **3**, 1982-1993 (2015).
5. A. Seki, Y. Funatsu, M. Funahashi, "Anomalous photovoltaic effect based on molecular chirality: Influence of enantiomeric purity on the photocurrent response in π-conjugated ferroelectric liquid crystals", *Phys. Chem. Chem. Phys*., **19**, 16446 - 16455 (2017).
6. A. Seki, M. Funahashi, " Chiral photovoltaic effect in an ordered smectic phase of a phenylterthiophene derivative", *Org. Electr*., **62**, 311-319 (2018).
7. M. Funahashi, "High open-circuit voltage in the bulk photovoltaic effect for the chiral smectic crystal phase of a double chiral ferroelectric liquid crystal doped with a fullerene derivative", *Mater. Chem. Front*., **5**, 8265–8274 (2021). [The artwork was adopted as an outside cover picture.]
8. M. Funahashi, Y. Mori, "Linearly polarized electroluminescence device in which the polarized plane can be rotated electrically using a chiral liquid crystalline semiconductor", *Mater. Chem. Front*., **4**, 2137-2148 (2020).