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Supporting Information

Dynamic Switching of Ionic Conductivity by Cooperative Interaction of Polyviologen and Liquid Crystals for Efficient Charge Storage

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EXPERIMETAL SECTION

Materials. 4-cyano-4'-pentylbiphenyl (5CB) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were obtained from Tokyo Kasei Co. ATO particles were purchased from Sigma-Aldrich Japan. Poly(vinylidene fluoride) (PVdF), was purchased from Kureha Chemical Co. Ionic liquids and supporting electrolytes 1-ethyl-3 methylimidazolium tris(pentafluoroethyl)trifluorophosphate(EMIM FAP), 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate(BMPL FAP), 1-ethyl-1-methylpyrrolidinium tetracyanoborate(EMIM TCB), 1-butyl-1-methylpyrrolidinium tetracyanoborate(BMPL TCB), tributylmethylphosphonium Bis(trifluoromethanesulfonyl)imide(TMP TFSI), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide(BMPL TFSI), tetrabutylammonium tetrafluoroborate(TBA BG_4), tetrabutylammonium perchlorate(TBA ClO_4), and other chemicals were provided by Merck, Sigma-Aldrich Japan, and Tokyo Kasei Co.

Synthesis of polyviologen 1. The polymer with tosylate salts was synthesized according to the previous procedure.[1] Then the counter ions were exchanged to hydrophobic TFSI in order to improve the affinity with 5CB and the response rate as the electrochromic devices. The aqueous solution of the polymer (2.07 g, 4.0 mmol) was dropped into excess amount of 2.0 M LiTFSI in water. The mixture was stirred for 2 h at room temperature. The precipitated product was dissolved in acetone, and the solution was re-precipitated in water. The polymer **1** was obtained after drying under vacuum overnight at room temperature as the amber adhesive solid (87% yield).

Fabrication and measurement of the electrochromic device. The electrochromic electrode was prepared by spin-coating 5 wt% acetone solution of **1** on an ITO substrate at 1500 rpm for one minute, and drying it under vacuum overnight. The counter electrode was prepared by the same procedure as electrochromic one using 2.5 wt% *N*-methylpyrrolidinone dispersion of ATO/PVdF = 95/5 (wt/wt) at 800 rpm (one minute) and then 2000 rpm (two minutes). The cell was fabricated by combining electrochromic and counter electrodes with a conventional hot-melt adhesive (thickness: 50 μm) followed by injecting electrolytes. Electrochemical characteristics were measured by a conventional potentiostat (PGSTAT 128N, AUTOLAB). Polarized optical microscopy and UV-Vis measurement were conducted by BX53 OLYMPUS and USB4000-UV-VIS Ocean Optics, respectively. Nematic-isotropic transition temperature of electrolytes were measured by differential scanning calorimetry (Q200 TA instrument). Measurement was conducted at room temperature. 1000 mT of external magnetic field was applied by sandwiching the cell with two conventional neodymium magnets (500 mT) obtained from KENIS LIMITED.

Selection and analyses of liquid crystal electrolytes for homeotropic alignment. Series of ionic liquids and conventional supporting electrolytes were mixed with 5CB, and the tendency of homeotropic alignment on ITO substrates were examined in symmetric sandwich cells (Table S1 and Fig. S1). Common ionic liquids such as 1-ethyl-3-Methylimidazolium tetrafluoroborate (EMIM BF_4) or 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6) were not miscible with 5CB presumably because of rather hydrophilic characteristics of anions. Homeotropic alignment against ITO was achieved with higher concentration of electrolytes containing specially hydrophobic anions FAP, TCB, and TFSI.[2–4] Ionic liquids with higher tendency for homeotropic alignment (i.e. FAP and TCB salts) exhibited higher ionic conductivity and lower nematic-isotropic transition temperature compared to other electrolytes (Fig. S2). Ionic conductivity was measured at 40 °C, which was higher than those of the phase transition with the 70 mM salt conditions and therefore enough to induce the isotropic phases (as a matter of fact, all electrolytes exhibited completely clear colour suggesting the isotropic phase at the temperature). The effect of anisotropic ion conduction can be sufficiently ignored by measuring at the isotropic phases. We assume that hydrophobic ionic liquids dissociate at high decree in 5CB, and it should result in the enhancement of (a) the electric field in diffusion layer inducing homeotropic alignment, (b) high ionic conductivity, and (c) decrease of the transition temperature because of the insulation of electrostatic interaction between liquid crystals. We selected 35 mM EMIM TCB in 5CB as an electrolyte for the electrochromic cell because it exhibited the most favourable property for switching alignment of liquid crystals along with charging/discharging. If the tendency for homeotropic alignment was too high (i.e. 75 mM), 5CB always aligns homeotropically even after charging of polyviologen because of the excess strength of electric field in the double layer, and the opposite occurs with electrolytes showing the lower tendency for homeotropic alignment.

Table S1. Alignment of 5CB with series of electrolytes ('+' and '-' symbol exhibit homeotropic and planar alignment, respectively)

Electrolyte	Homeotropic alignment					Conductance (mS/cm)[a]
	0 mM	10 mM	20 mM	35 mM	70 mM	
EMIM FAP	-	+	+	+	+	0.78
BMPL FAP	-	+	+	+	+	0.65
EMIM TCB	-	-	-	+	+	0.64
BMPL TCB	-	-	-	-	+	0.66
TMP TFSI	-	-	-	-	+	0.27
BMPL TFSI	-	-	-	-	-	0.36
TBA BF_4	-	-	-	-	-	0.14
TBA ClO_4	-	-	-	-	-[b]	-[b]

[a]Measured with comb-shaped electrodes at 70 mM and 40°C, [b]Insoluble.

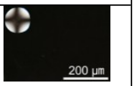
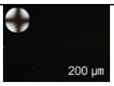
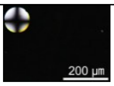
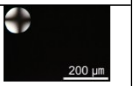
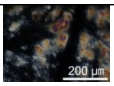
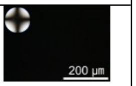
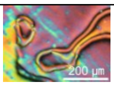
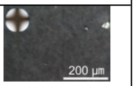
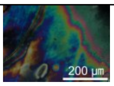
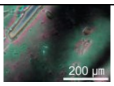
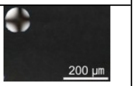
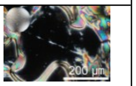
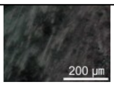
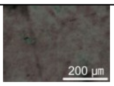
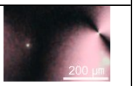
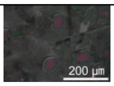
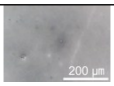
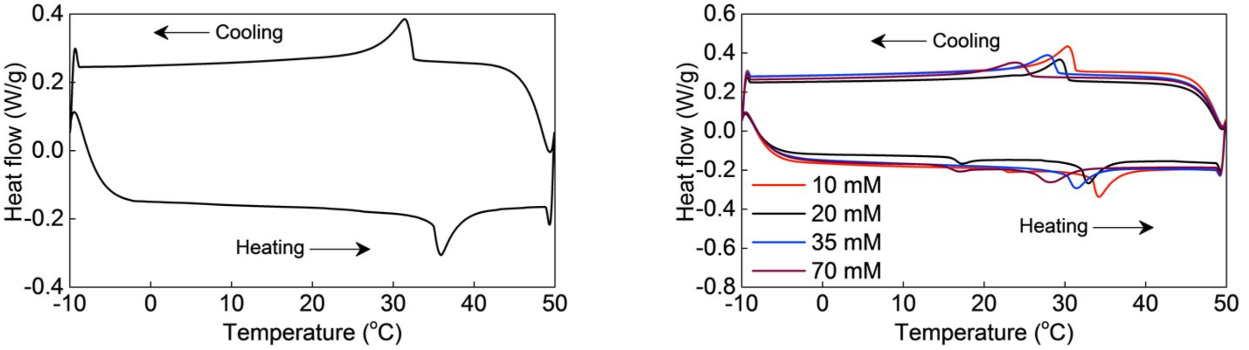
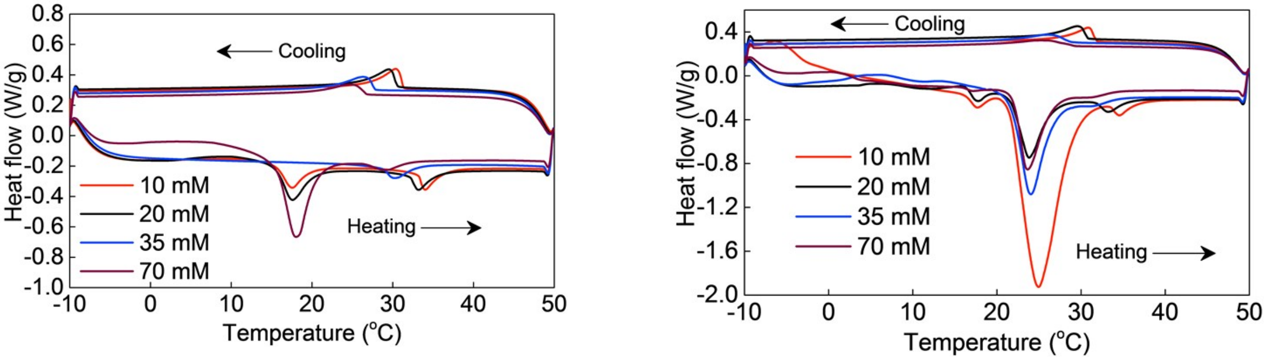
Electrolyte	Concentration (mM)			
	10	20	35	70
EMIM FAP				
BMPL FAP				
EMIM TCB				
BMPL TCB				
TMP TFSI				
BMPL TFSI				
TBA BF_4				
TBA ClO_4				*Insoluble*

Figure S1 Alignment of liquid crystal electrolytes against ITO substrates.



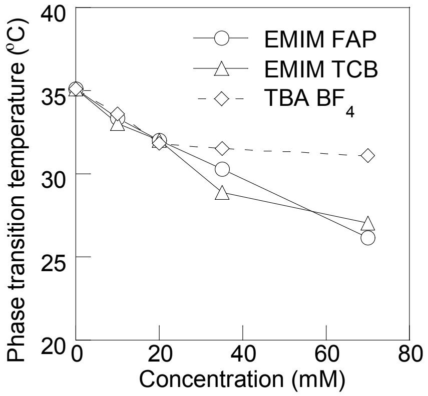
(a) 5CB

(b) EMIM FAP + 5CB



(c) EMIM TCB + 5CB

(d) TBA BF$_4$ + 5CB



(e) Phase transition temperature

Figure S2 Thermal properties of liquid crystal electrolytes. (a)-(d) DSC thermograms scanned at 10 ^{o}C/min measured by Q200 (TA Instruments). Endothermic and exothermic peaks at 25-40 ^{o}C should correspond to those of the phase transition. Endothermic peaks near 17 ^{o}C can be assigned to melting of 5CB electrolytes, and peaks near 24 ^{o}C with the TBABF$_4$ conditions should be originated from dissolution of the salts. (e) Nematic-isotropic transition temperature of the electrolytes estimated by DSC thermograms.

Electrochemical properties of 35 mM EMIM TCB in 5CB. Ionic conductivity of the electrolyte was measured by sandwiching it with ITO substrates (Fig. S3). Planar alignment was induced by applying 1000 mT magnetic field. Conductivities were calculated to be 1.48 x10^{-5} and 1.66 x10^{-5} S/cm for planar and homeotropic alignment, respectively (ratio: 1.13).

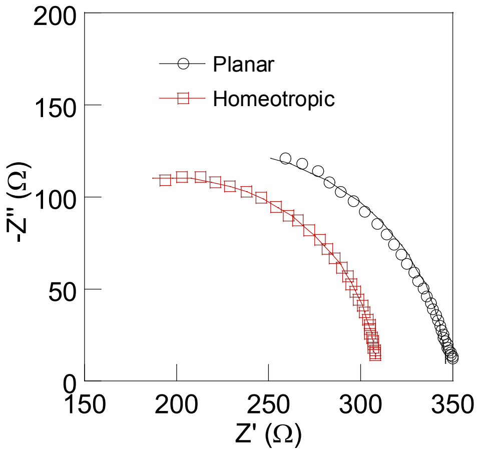


Figure S3 Electrochemical impedance spectra of 35 mM EMIM TCB in 5CB solution with planar and homeotropic alignment (10^6 to 5 x10^4 Hz, AC amplitude 10 mV).

References

1 R. H. Terrill, J. E. Hutchison and R. W. Murray, *J. Phys. Chem. B*, 1997, **101**, 1535–1542.
2 N. V Ignat'ev, U. Welz-Biermann, a. Kucheryna, G. Bissky and H. Willner, *J. Fluor. Chem.*, 2005, **126**, 1150–1159.
3 T. Küppers, E. Bernhardt, H. Willner, H. W. Rohm and M. Köckerling, *Inorg. Chem.*, 2005, **44**, 1015–1022.
4 H. Kato, K. Nishikawa and Y. Koga, *J. Phys. Chem. B*, 2008, **112**, 2655–2660.