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Supporting Information

Piezochromic Fluorescence in Liquid Crystalline Conjugated Polymers

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Experimental Methods

1) Materials:

The syntheses of 1–3 were already reported in previous paper.¹ The polymers used in this study have high weight-average molecular weights (M_w) of 4.18 x 10⁶, 7.54 x 10⁶ and 5.23 x 10⁶ g/mol, respectively, and polydispersity indices ($PDI = M_w/M_n$) of 2.5, 1.8 and 3.2, respectively.

2) Preparation of polymer solution, solvent cast film (SC-film), mechanically processed film (MP-film), and KBr pellets:

The polymers were dissolved in toluene to prepare highly dilute solutions with a concentration of less than 1.0×10^{-6} M. The polymers were dissolved in toluene to prepare films with thickness of about 30 µm by using solvent casting method. The bulk solids of the polymers were manually ground in a mortar and subsequently pressed by glass roller in order to prepare films with thickness of about 100 µm. The bulk solids of the polymers were mixed with KBr powder and then manually ground in a mortar and subsequently pressed at 400 kg/m² by a press machine in order to prepare KBr pelltes with thickness of about 750 µm.

3) Measurements:

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of **1–3** were evaluated using gel permeation chromatography (GPC, Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column,

and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. Fluorescence spectra were recorded on a JASCO ETC-273 spectrofluorometer. Polarizing optical microscope (POM) images were recorded on a Nikon Eclipse E600 POM equipped with a Nikon DS-Fi1 digital camera. The fluorescence images were taken with a Cannon PowerShot A2000IS. XRD measurements were performed at room temperature using a X-ray diffracter (PANalytical X`Pert PRO-MPD) in Korea Basic Science Institute (Daegu). The samples were mounted directly into the diffractor. The experiment was carried out using $CuK_{\alpha}(1.54\text{\AA})$ radiation operating at 40kV and 25mA. For measuring exciton lifetimes, Time-Correlated Single Photon Counting (TCSPC) was performed. The second harmonic (SHG = 420 nm) of a tunable Ti:sapphire laser (Mira900, Coherent) with \sim 150 fs pulse width and 76MHz repetition rate was used as an excitation source. The PL emission was spectrally resolved by using some collection optics and a monochromater (SP-2150i, Acton). The TCSPC module (PicoHarp, PicoQuant) with a MCP-PMT (R3809U-59, Hamamatsu) was used for ultrafast detection. The total instrument response function (IRF) for PL decay was less than 100 ps, which provided the temporal resolution less than 10 ps. The deconvolution of actual fluorescence decay and IRF was performed by using a fitting software (FlouFit, PicoQuant) to deduce the time constant associated with each exponential decay.

References

1) T. Sakaguchi, K. Yumoto, M. Shiotsuki, F. Sanda, M. Yochikawa, T. Masuda, *Macromolecules* **2005**, *38*, 2704-2709.





Fig. S2 FL decay profiles of **1**, **2**, and **3** in the SC- and MP-films (powders). (excited at 420nm; monitored at 520nm)





Fig. S3 WAXD patterns of 1 in the SC-film (film thickness $\sim 30~\mu m)$ and the MP-film (film thickness ~ 100 μ m). Inset : POM images.







