Electronic Supplementary Information

Fluorescence enhancement induced by quadratic electric-field effects on dynamics of singlet exciton in poly(3-hexylthiophene) dispersed in poly(methyl methacrylate)

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1. Electroabsorption (E-A) and electro-photoluminescence (E-PL) spectroscopy

In electroabsorption (EA) measurements, we used a commercial spectrometer (EMV-100, JASCO).[1] The sinusoidal alternating current (AC) voltage of 1 kHz was generated by a function generator (SG-4311, Iwatsu), amplified by a high voltage amplifier, and applied to the electrodes of the substrate. A linearly polarized light was transmitted the substrate and the field-induced change in the transmitted light intensity was detected with a lock-in amplifier (Stanford Research System, SR830) at the second harmonic of the modulation frequency. A direct current component of the transmitted light intensity was simultaneously monitored. The change in absorption intensity (ΔA) was calculated from the field-induced change and DC component of the transmitted light intensity. EA spectra were obtained by plotting ΔA as a function of wavelength. The angle between the direction of the applied electric field and the electric vector of the excitation light was set to be 54.7° in the EA measurements. Applied field strength was evaluated from the applied voltage divided by the thickness of the film.

Electro-photoluminescence (E-PL) spectra were measured with a commercial spectrofluorometer (JASCO, FP777) which was combined with a lock-in amplifier.[2] In this work, E-PL spectra were obtained with excitation at wavelengths at which the field-induced change in absorption intensity was negligibly small. The sample substrate was kept under vacuum, and the incident angle of the light on the substrate was 45°. The frequency of the applied voltage was 40 Hz in the E-PL measurements. The modulation signal in the PL intensity was detected with the lock-in amplifier at the second harmonic of the modulation frequency.

2. Time-resolved electro-photoluminescence measurements

The details of the setup of the system have been reported elsewhere.[3] A mode-locked Ti: sapphire laser (Tsunami, Spectra Physics) pumped by a diode laser (Millennia Xs, Spectra Physics) was used as an excitation light source. The repetition rate of the laser pulse, which was originally 80 MHz, was reduced with an electro-optic modulator (model 350-160, Conoptics). The second harmonic generation (SHG) or third harmonic generation (THG) generated by an ultrafast harmonic system (Inrad, model 5-050) was used for excitation. The excitation laser pulse was monitored by a high speed photodiode. The discriminated signal of the excitation laser pulse, which was led to a time-to-amplitude converter (TAC) (EG&G Ortec) with a delay time, was used as a stop pulse. Emission from a sample was dispersed by a monochromator (G-250, Nikon), and detected by a multi-channel plate photomultiplier (Hamamatsu R-3809U-52) in a single-photon counting mode. The emission photon pulse was amplified by an AC-coupled high-speed preamplifier, discriminated, and then fed to the TAC as a start pulse. We used a multichannel pulse height analyzer (MCA) (Seiko EG&G 7700) to accumulate the output of the TAC, and emission decay profiles were obtained from the data of the MCA. The instrument response function had a pulse width of ~60 ps full width at half maximum.

The memory of the MCA was divided into four segments, which were denoted by SEGMENT1, SEGMENT2, and so on in Fig. S1. From the four memory segments of the MCA, we were able to obtain decay profiles in the presence of positive, zero, negative, and zero bias voltages, respectively. When electric field whose strength is 0.3 $MVcm^{-1}$ is applied, for example, PL decay profiles in the presence of +0.3, 0, –0.3, 0 $MVcm^{-1}$, respectively, are obtained in SEGMENTs 1 - 4. The data at SEGMENTs 1 - 4 are denoted by Channels 1 – 4, respectively, i.e., (CH1 - CH4) in the text. CH1 and CH3, which correspond to the decays in the presence of +0.3 and –0.3 $MVcm^{-1}$, respectively, are shown in the text (Figs. 5 and 6). As shown in Fig. S2, the ratio between CH2 and CH4, both of which correspond to the decay at

zero field, is unity in the whole time region, indicating that both decays are essentially the same. The time duration of each segment (i.e., the duration of the voltage pulse) was 30 ms.
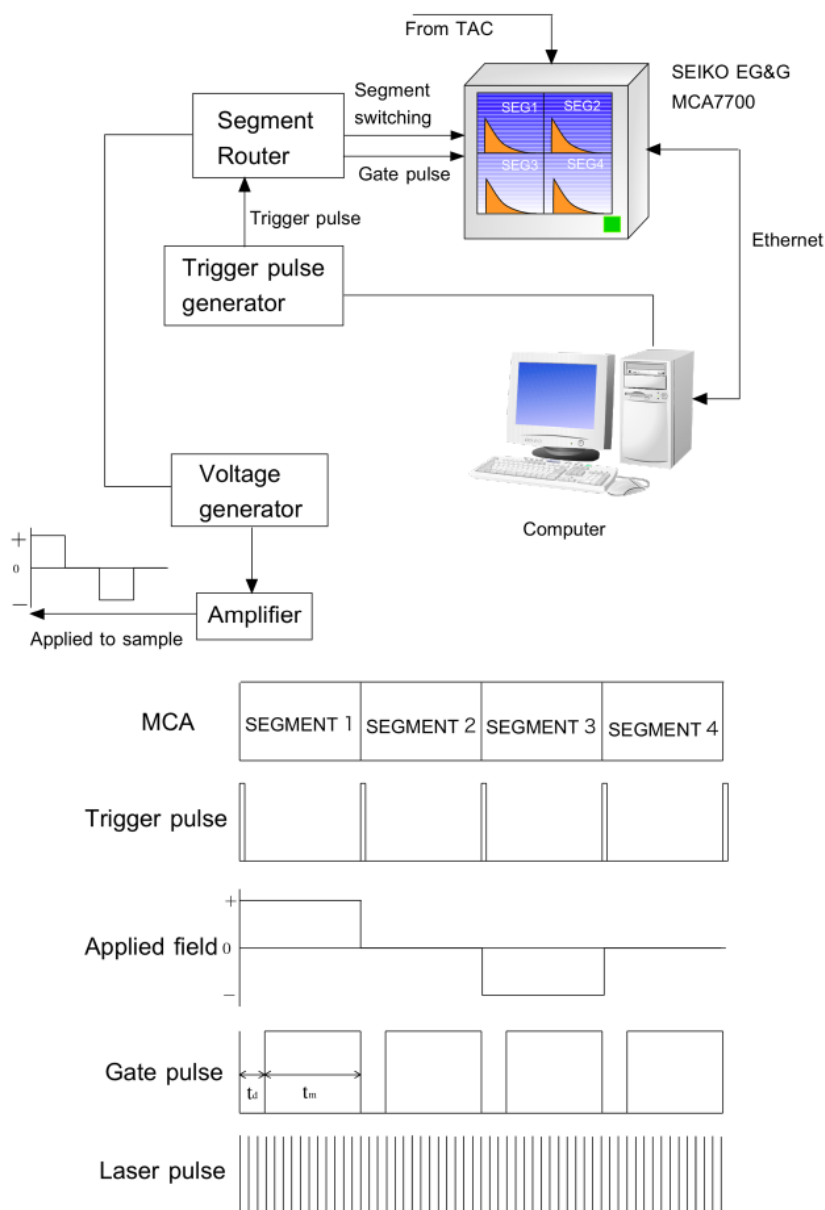

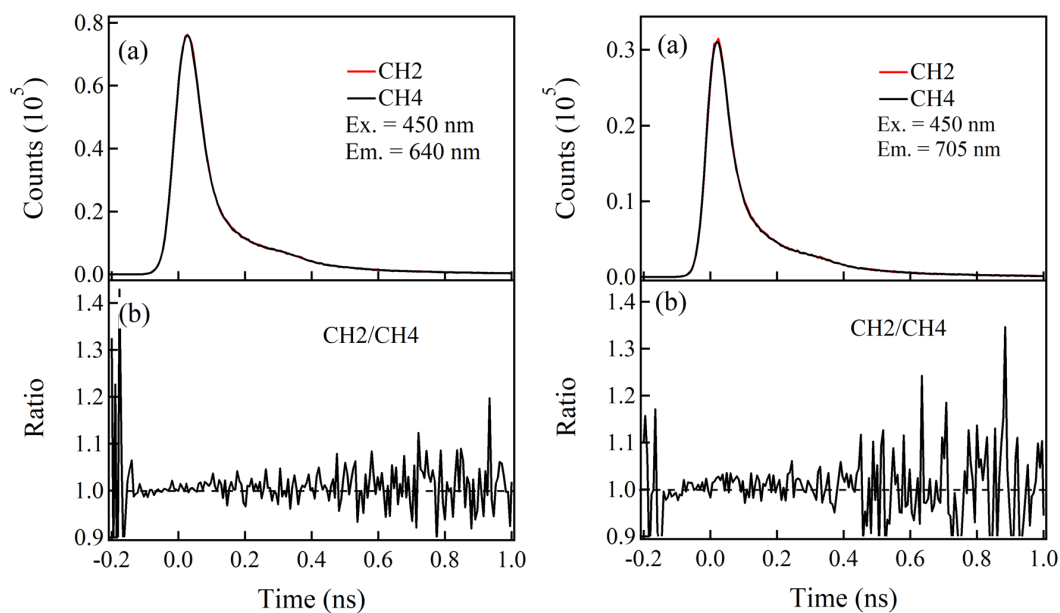Fig. S1. Setup and timing chart of time-resolved E-PL system.[3]

Fig. S2. PL decay profiles of P3HT dispersed in a PMMA matrix. (a) Decay profiles observed at zero field (CH2 and CH4), and (b) ratio between decay profiles observed at zero field, i.e., CH2 and CH4. The results in the left and in the right were obtained by monitoring PL at 640 nm and 705 nm, respectively. These decays were observed at the same time with the decays shown in Figs. 5-7 of the text.

References

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2   N. Ohta, *Bull. Chem. Soc. Jpn.,* 2002, **75**, 1637-1655.

3   M. Tsushima, T. Ushizaka, N. Ohta, *Rev. Sci. Instrum.*, 2004, **75**, 479-485.