Supporting Information

Time-resolved Fluorescence Spectra in the End-Functionalized Conjugated Triblock Copolymers Consisting of Poly(fluorene vinylene) and Oligo(phenylene vinylene):

Proposal of Dynamical Distortion in the Excited State

Motoko S. Asano, *^{1,2,3} Daichi Kagota,² Tahmina Haque,² Misaki Koinuma,¹ Akiko Inagaki² and Kotohiro Nomura*^{,2,3}

¹Division of Molecular Science, School of Science and Engineering, Gunma University, 1-5-1, Ten-jincho, Kiryu, Gunma 376-8515, Japan, ²Department of Chemistry, School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0376, Japan, ³Advanced Catalytic Transformation for Carbon Utilization (ACT-C), Japan Science and Technology Agency (JST), Saitama 332-0012,

Japan

*Corresponding Authors, tel.: +81-277-30-1902, E-mail: motoko@gunma-u.ac.jp,

tel.&fax: +81-42-677-2547, E mail: ktnomura@tmu.ac.jp

Contents

1. Plots of emission intensities vs. absorbance

Figure S1 – Figure S4

- Concentration dependence of emission, absorption and excitation spectra Figure S5 – Figure S9
- Effects of Ar bubling on absorption, emission and excitation spectra Figure S10 – Figure S11
- Concentration dependence of fluorescence decay time profiles
 Figure S12 Figure S13
- Selected data of two dimensional time-resolved fluorescence signals Figure S14
- Time-resolved fluorescence signals including band II
 Figure S15–16
- Viscosity dependence of fluorescence decay time profiles
 Figure S17
- 8. Additional data for an end-functionalized tri-block copolymer, consisting of PFVs and OPVs having terthiophene as the end-groups

Figure S18–20

1. Plots of emission intensities vs. absorbance

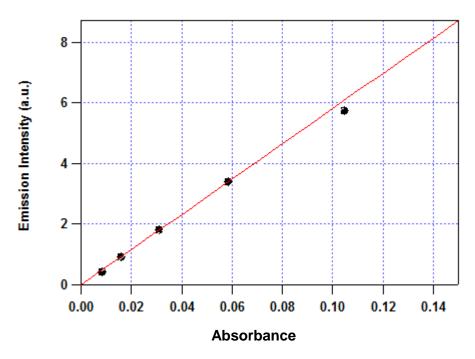


Figure S1. Plots of emission intensities vs. absorbance for $[10PFv-7Pv]P_2$ in toluene. Intensities plotted were at the maximum of the visible band both in emission and absorption spectra.

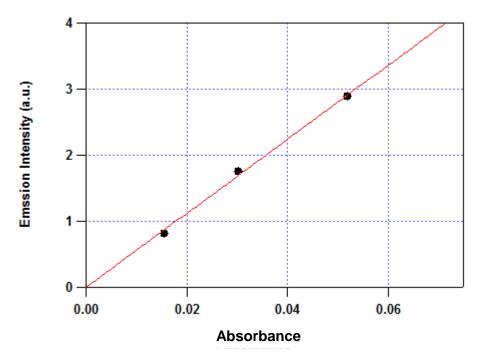


Figure S2. Plots of emission intensities vs. absorbance for $[10PFv-7Pv]F_2$ in toluene. Intensities plotted were at the maximum of the visible band both in emission and absorption spectra.

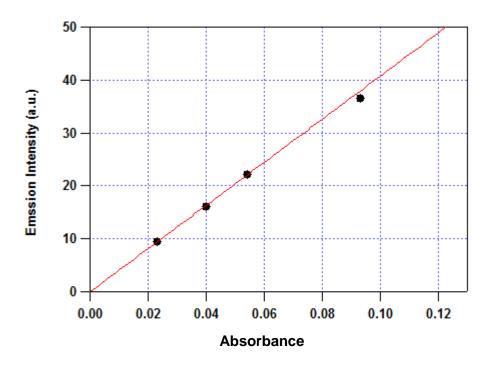


Figure S3. Plots of emission intensities vs. absorbance for $[20PFV-7PV]P_2$ in toluene. Intensities plotted were at the maximum of the visible band both in emission and absorption spectra.

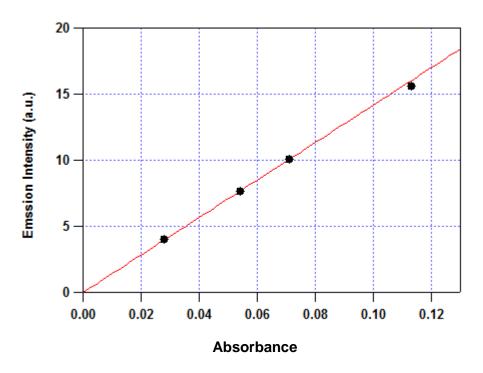


Figure S4. Plots of emission intensities vs. absorbance for $[10PFV-3PV]F_2$ in toluene. Intensities plotted were at the maximum of the visible band both in emission and absorption spectra.

2. Concentration dependence of emission, absorption and excitation spectra

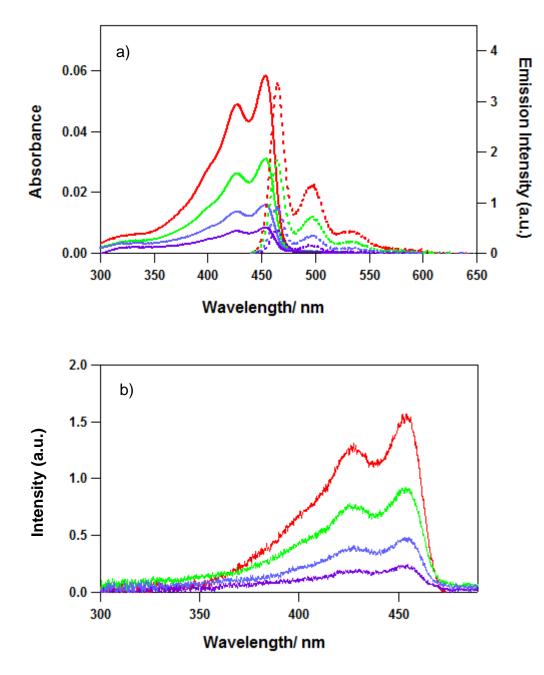


Figure S5. Concentration dependence of a) emission (-----) and absorption (-----) spectra and b) excitation spectra for [10PFV-7PV]P₂ in toluene.

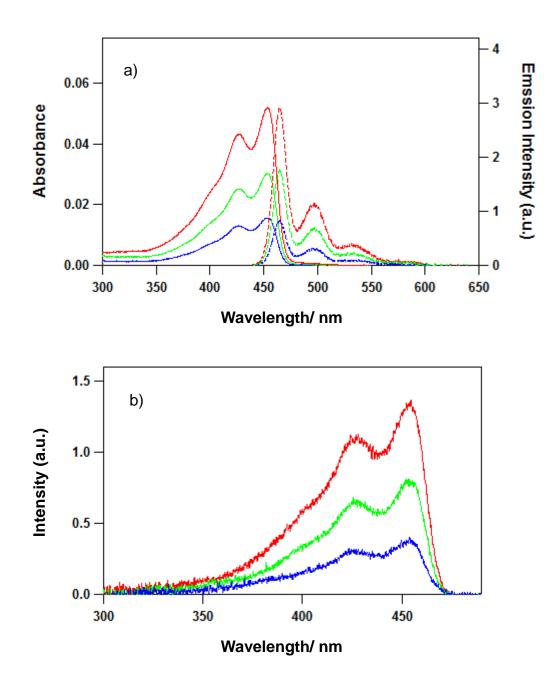


Figure S6. Concentration dependence of a) emission (-----) and absorption (-----) spectra and b) excitation spectra for $[10PFV-7PV]F_2$ in toluene.

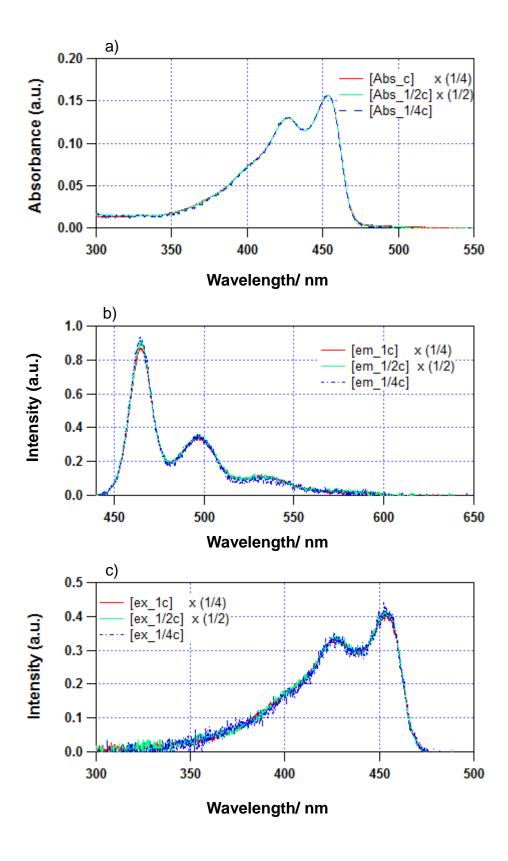


Figure S7. Concentration dependence of a) absorption, b) emission and excitation spectral profiles for $[10PFV-7PV]F_2$ in toluene. Intensities are normalized in each figure (normalization factors were given in figures).

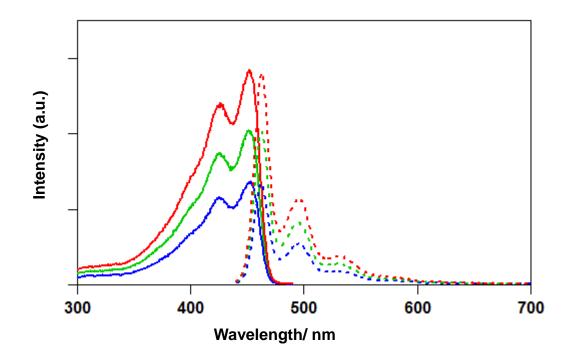


Figure S8. Concentration dependence of a) emission (-----) and excitation (_____) spectra and b) spectra for [20PFV-7PV]P₂ in toluene.

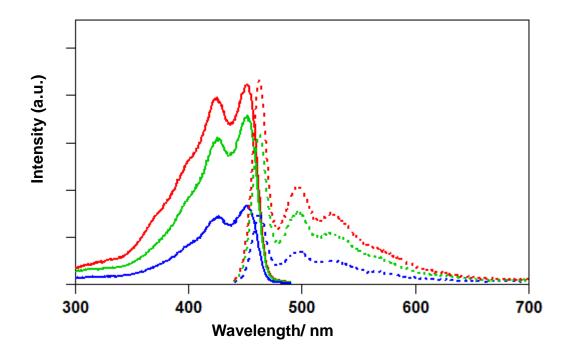
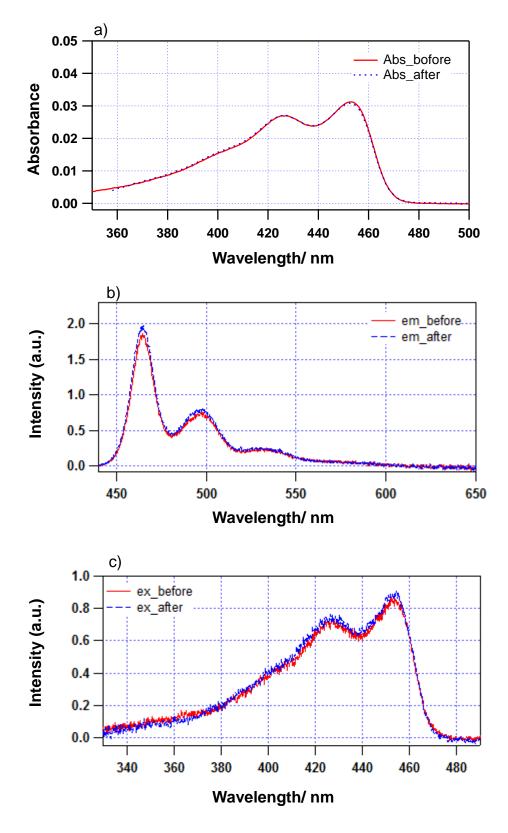


Figure S9. Concentration dependence of a) emission (-----) and excitation (----) spectra and b) spectra for [10PFV-3PV]F₂ in toluene.



3. Effects of Ar bubling on absorption, emission and excitation spectra

Figure S10. a) absorption, b) emission and c)excitation spectra before and after Ar bubling of toluene solution of $[10PFV-7PV]P_2$.

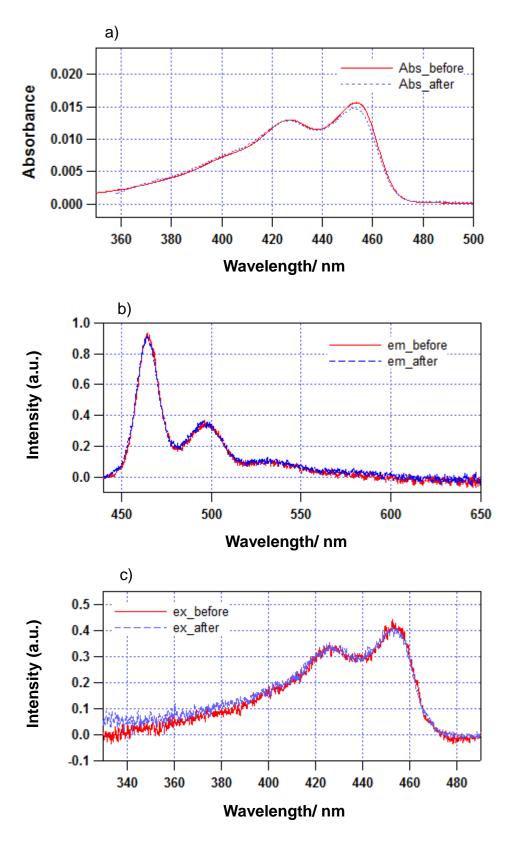
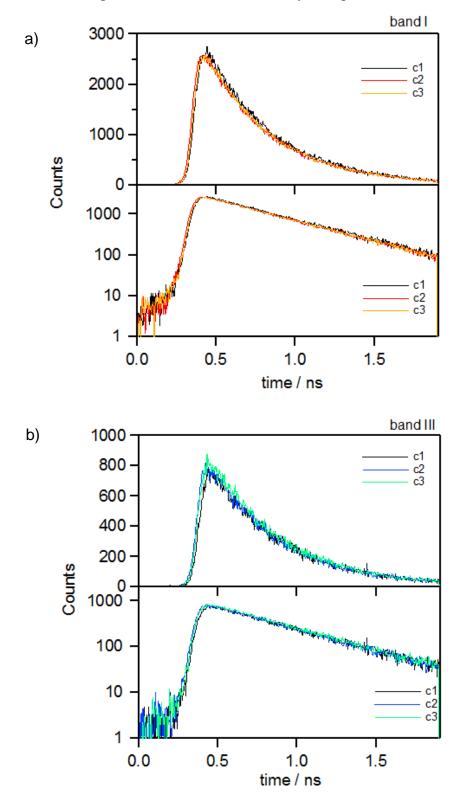


Figure S11. a) absorption, b) emission and c)excitation spectra before and after Ar bubling of toluene solution of $[10PFV-7PV]F_2$.



4. Concentration dependence of fluorescence decay time profiles

Figure S12. Time-resolved fluorescence signals for $[10PFV-7PV]F_2$ in toluene excited at 406 nm. Monitored at a) band I and b) band III. Absorbance at 454 nm (400 nm) of solutions in a 2mm path-length cell are 0.094(0.041), 0.039(0.017) and 0.018(0.008) for c1, c2 and c3, respectively.

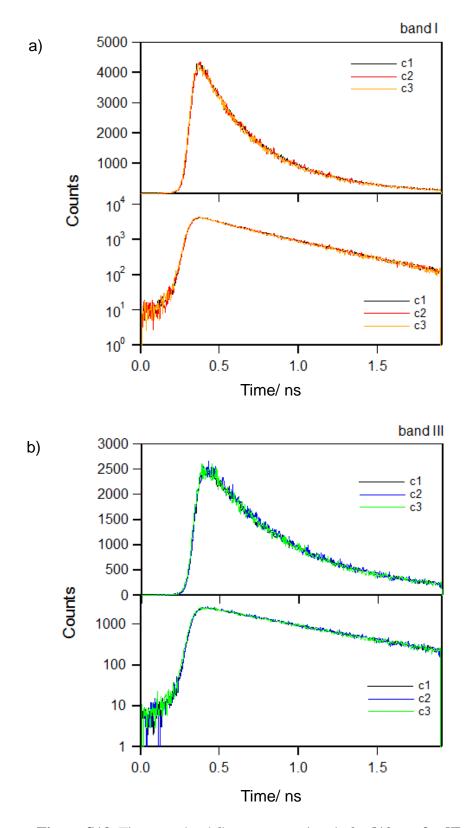


Figure S13. Time-resolved fluorescence signals for $[10PFV-3PV]F_2$ in toluene excited at 406 nm. Monitored at a) band I and b) band III. Absorbance at 454 nm (400 nm) of solutions in a 2mm path-length cell are 0.098(0.043), 0.040(0.017) and 0.020(0.009) for c1, c2 and c3, respectively.

5. Selected data of two dimensional time-resolved fluorescence signals

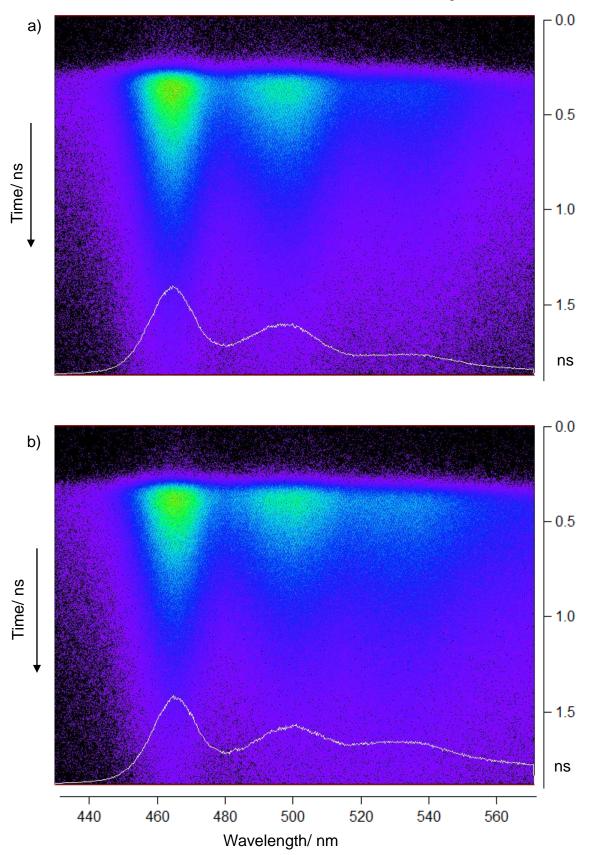


Figure S14. Image data of time-resolved fluorescence signals for a) $[10PFV-7PV]F_2$ and b) $[10PFV-3PV]F_2$ in toluene. Experimental conditions are in text.

6. Time-resolved fluorescence signals including band II

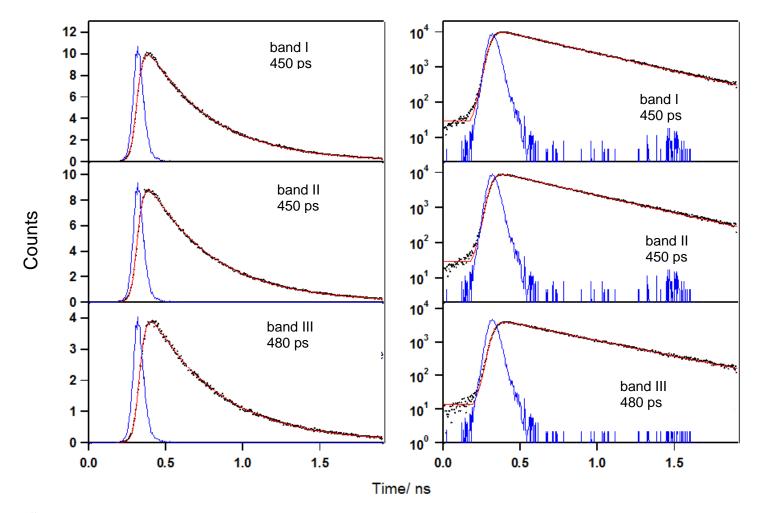


Figure S15. Time-resolved fluorescence signals monitored at band I, II and band III for $[10PFv-7Pv]F_2$ in toluene with excitation at 406 nm. Figures in right hand side are in semilogarithmic scale. The observed signals are in dots while fits are presented in red solid lines. Blue lines correspond to excitation laser responses.

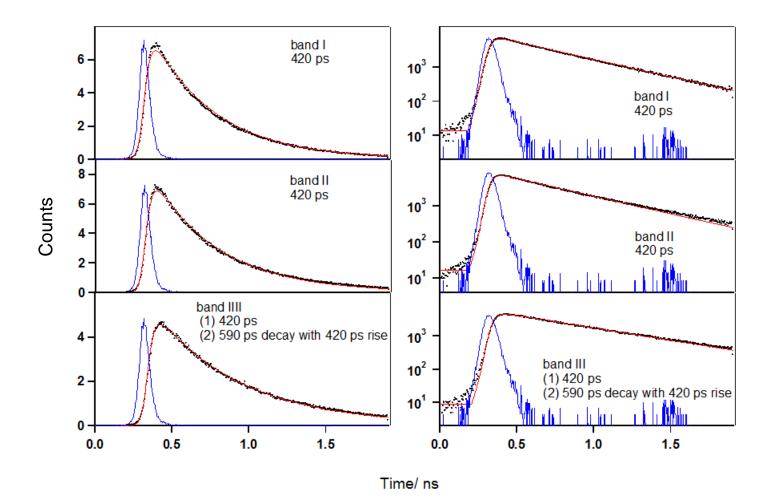


Figure S16. Time-resolved fluorescence signals monitored at band I, II and band III for $[10PFV-3PV]F_2$ in toluene with excitation at 406 nm. Figures in right hand side are in semilogarithmic scale. The observed signals are in dots while fits are presented in red solid lines. Blue lines correspond to excitation laser responses.

7. Viscosity dependence of fluorescence decay time profiles

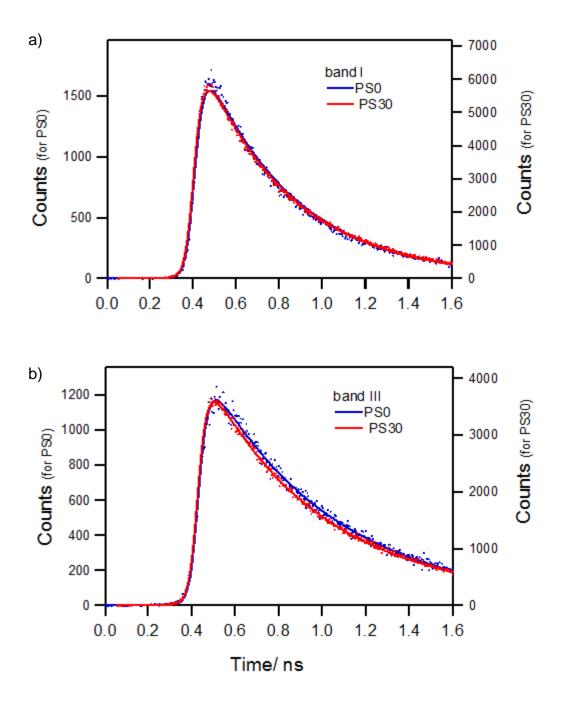
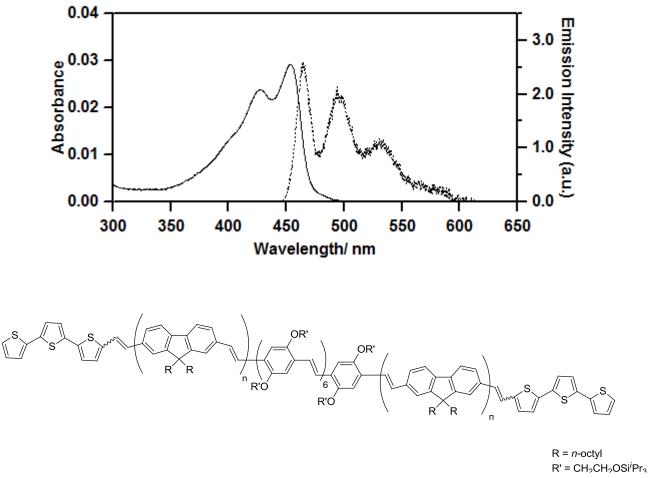


Figure S17. Time-resolved fluorescence signals monitored at a) band I and b) band III for $[10PFV-3PV]F_2$. Data and its fit in toluene are in blue whereas those in toluene/polystyrene are in red.

8. Additional data for an end-functionalized tri-block copolymer, consisting of PFVs and OPVs having terthiophene as the end-groups



n ~ 10

 $[10PFV-7PV](3T)_2$

Figure S18. Absorption (——) and emission (-----) spectra for $[10PFV-7PV](3T)_2$ in toluene. Identifications of the sample are given in the previous report. ^{22a)}

Reference

(22) (a) Nomura, K. ; Haque, T.; Onuma, T.; Hajjaj, F.; Asano, M. S.; Inagaki, A. *Macromolecules*, **2013**, *46*, 9563.

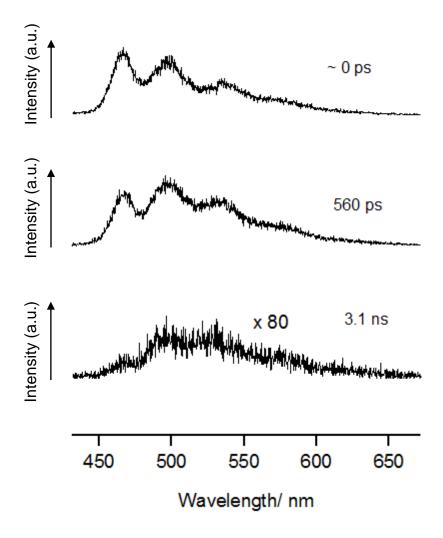


Figure S19. Time-resolved fluorescence spectra of $[10PFV-7PV](3T)_2$ in toluene excited at 406 nm. The upper spectra were taken just after the laser pulse and the middle and lower spectra were taken at delay times 560 ps and 3.1 ns, respectively. Other experimental conditions are the same as those in Figure 3.

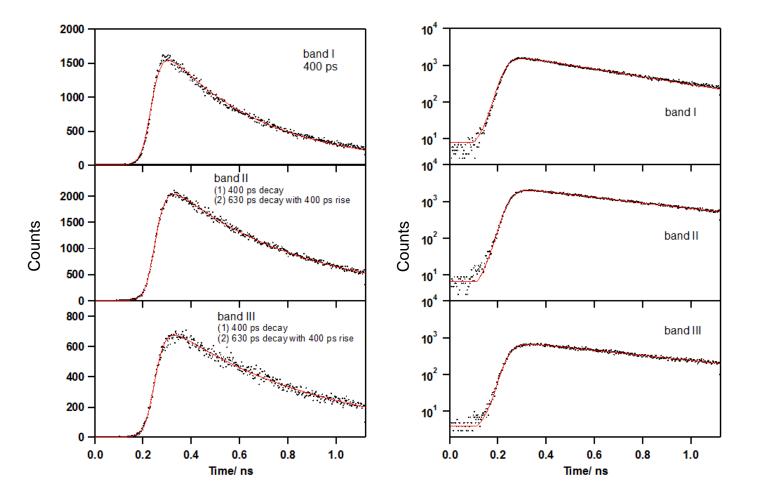


Figure S20. Time-resolved fluorescence signals of $[10PFV-7PV](3T)_2$ in toluene with excitation at 406 nm. Figures in right hand side are in semilogarithmic scale. The observed signals are in dots while fits are presented in red solid lines. experimental conditions are the same as those in Figure 2.