Supplemental material

Interaction between the End Groups and the Main Chain of Conjugated

Polymers by Time-Resolved EPR and Fluorescence Spectroscopy

Motoko S. Asano,* Sho Hashimoto, Takuya Shinozuka, Yasutaka Fushimi and

Kotohiro Nomura*

Division of Molecular Science, Graduate School of Science and Technology, Gunma University, 1-5-1, Ten-jincho, Kiryu, Gunma 376-8515, Japan Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachi-Ohji, Tokyo 192-0397, Japan

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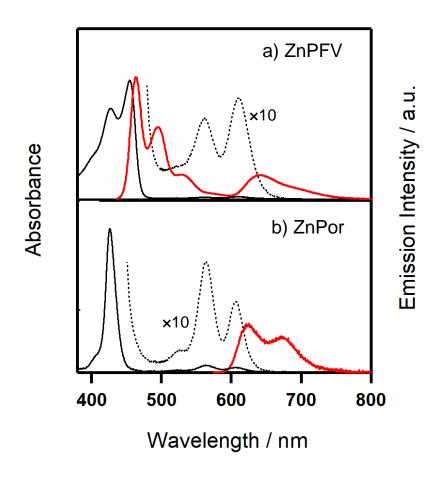


Figure S1. Absorption and emission spectra of ZnPFV and ZnPor in 2mTHF. Black solid lines stand for absorption spectra and dashed lines are expanded absorption spectra. Red lines are for fluorescence spectra.

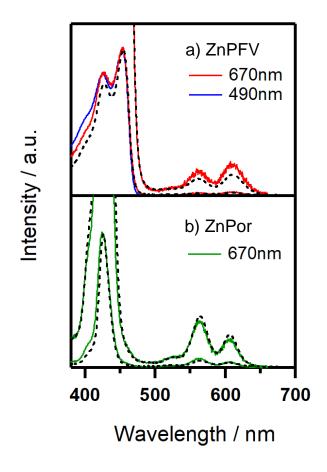


Figure S2. Excitation spectra in 2mTHF of a) ZnPFV monitored at 670 nm and 490nm, b) ZnPor monitored at 670 nm. Solid lines are excitation spectra whereas dashed lines are absorption spectra. The ordinate of excitation spectrum was normalized to fit the absorption spectrum in each wavelength region.

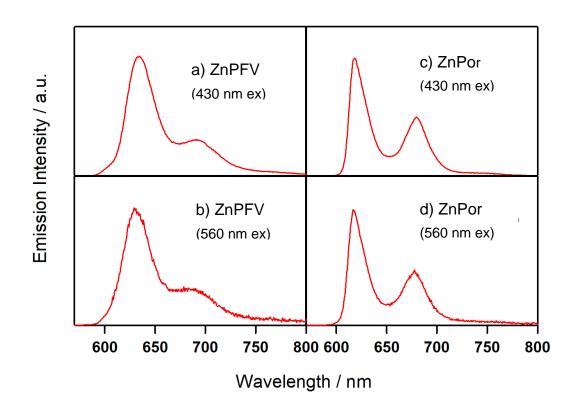


Figure S3. Steady state emission spectra in 2mTHF at 77K of a) ZnPFV excited at 430 nm, b) ZnPFV excited at 560 nm, c) ZnPor excited at 430 nm and d) ZnPor excited at 560nm.

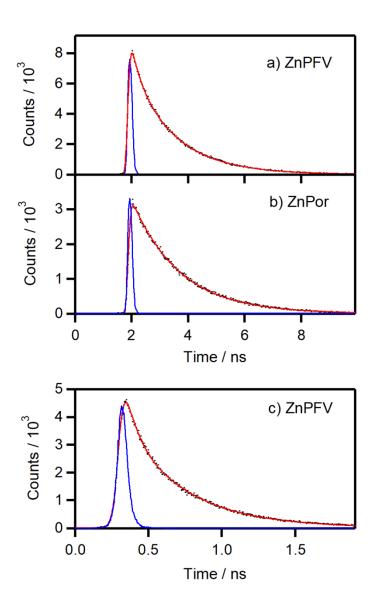


Figure S4. Time-resolved fluorescence signals of a) ZnPFV monitored at 660 nm, b) ZnPor monitored at 660 nm and c) ZnPFV monitored at 500 nm in THF, together with the instrumental responses. Excitation was done at 406 nm (FWHM = 70 ps). Dots are observed signals and fits are in solid line. For the fitting functions and obtained parameters were given in the foot note of Table S1.

Sample	Time scale	Band	τ_1 / ns	A_1	τ_2/ns	A_2	χ^2	Wavelength at the band maximum
ZnPFV	2 ns	PFV-I ^{b)}	0.060	0.048	0.410	0.060	1.15	462 nm
		PFV-II ^{b)}	0.060	0.047	0.410	0.060	1.09	494 nm
		PFV-III ^{b)}	0.060	0.025	0.400	0.034	1.24	532 nm
	10 ns	PFV-Por ^{b)}	1.52	0.32	0.400	0.096	1.12	640 nm
ZnPor	10 ns	Por-I ^{c)}	1.68	0.15	-	-	1.11	624 nm
	10 ns	Por-II ^{c)}	1.68	0.12	-	-	1.10	673 nm

Table S1.Fluorescence decay parameters ^{a)} of ZnPFV and ZnPor in THF

^{a)} Fitting procedure was carried out by using a convoluted function of this decay function with an instrumental response, i.e., the excitation pulse profile.

^{b)} A double exponential function, $y = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2)$, was used.

^{c)} A single exponential decay function, $y = A_1 \exp(-t / \tau_1)$ was used.

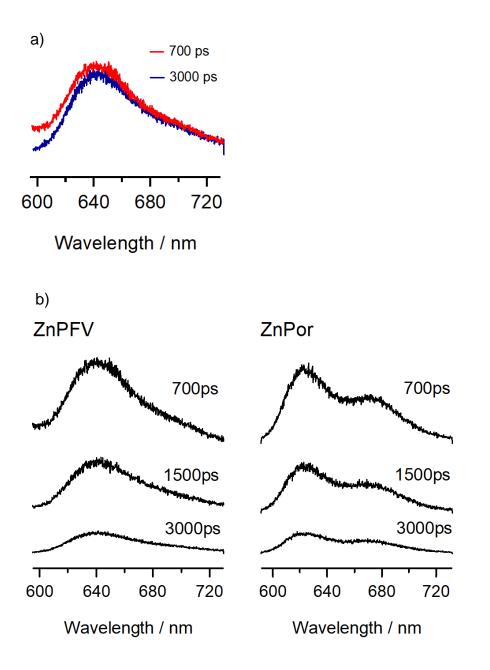


Figure S5. a) Comparison of time-resolved fluorescence spectra of ZnPFV taken at the delay times of 700 ps and 3000 ps in THF. In the 700 ps spectrum, broad background signal was overlapped. b) Comparison of time-resolved fluorescence spectra of ZnPFV (left) and the reference ZnPor (right). In the reference ZnPor, there was no back ground signal.