Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intrachain Photophysics of a Donor−Acceptor Copolymer

Hak-Won Nho,[a,b†] *Won-Woo Park,*[a†] *Byongkyu Lee,*[c†] *Seoyoung Kim,*[c] *Changduk Yang,*[*c] *and Oh-Hoon Kwon*[*a,b]

[a]Department of Chemistry, College of Natural Sciences, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea.

[b]Center for Soft and Living Matter, Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea

[c]Department of Energy Engineering, School of Energy and Chemical Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, Republic of Korea.

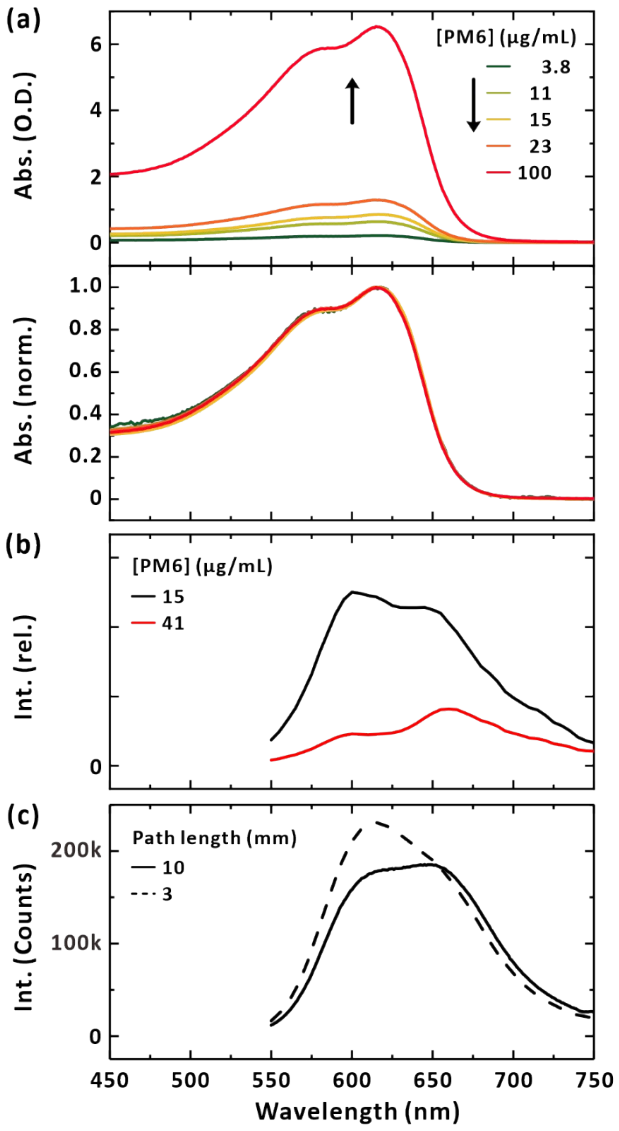

Fig. S1. Self-absorption of photoluminescence (PL). (a) Concentration-dependent absorption spectra. Concentrations are given in the panel. Area-normalized absorption spectra are also presented for comparison in the bottom panel. The absorption spectra show the same spectral feature regardless of the concentrations. (b) Scaled PL spectra of the [PM6] = 15 μg/mL and [PM6] = 41 μg/mL samples. The PL intensity is normalised to the absorbance of the samples at the excitation wavelength of 510 nm. (c) Dependence of PL spectra on the optical path

length. M_n = 14.9 kDa. [PM6] = 15 μg/mL. With an increase of the path length, the self-absorption of the blue side of the spectrum is evident.

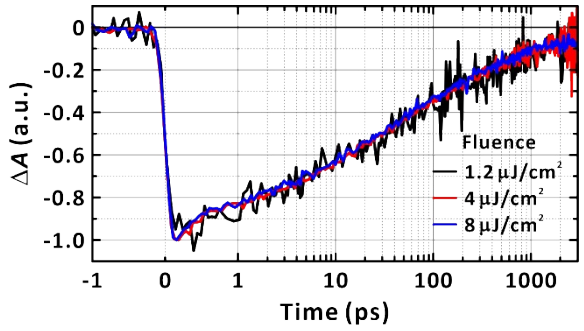

Fig. S2. Dependence of ground-state bleach (GSB) recovery on fluence. M_n = 40.3 kDa. [PM6] = 15 μg/mL. Excitation wavelength is 570 nm. Representative excitation fluences are given in the panel. Up to the highest fluence (8 μJ/cm^2), normalized kinetic profiles measured for GSB overlap with each other after 1 ps. With the fluence of 4 μJ/cm^2 and higher, an ultrafast component starts to emerge indicating a small fraction of locally excited (LE) state are annihilated via bimolecular processes. The ultrafast component is absent with the fluence of 1.2 μJ/cm^2.

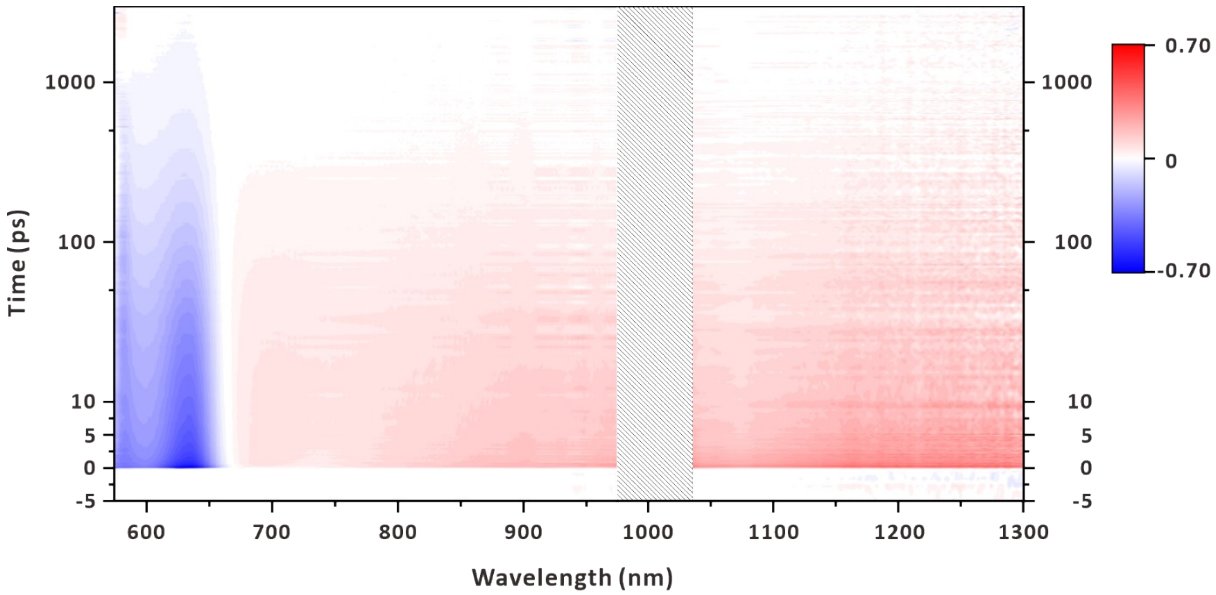

Fig. S3. Color-coded two-dimensional transient-absorption (TA) map upon the excitation at 570 nm. M_n = 40.3 kDa. [PM6] = 15 μg/mL.

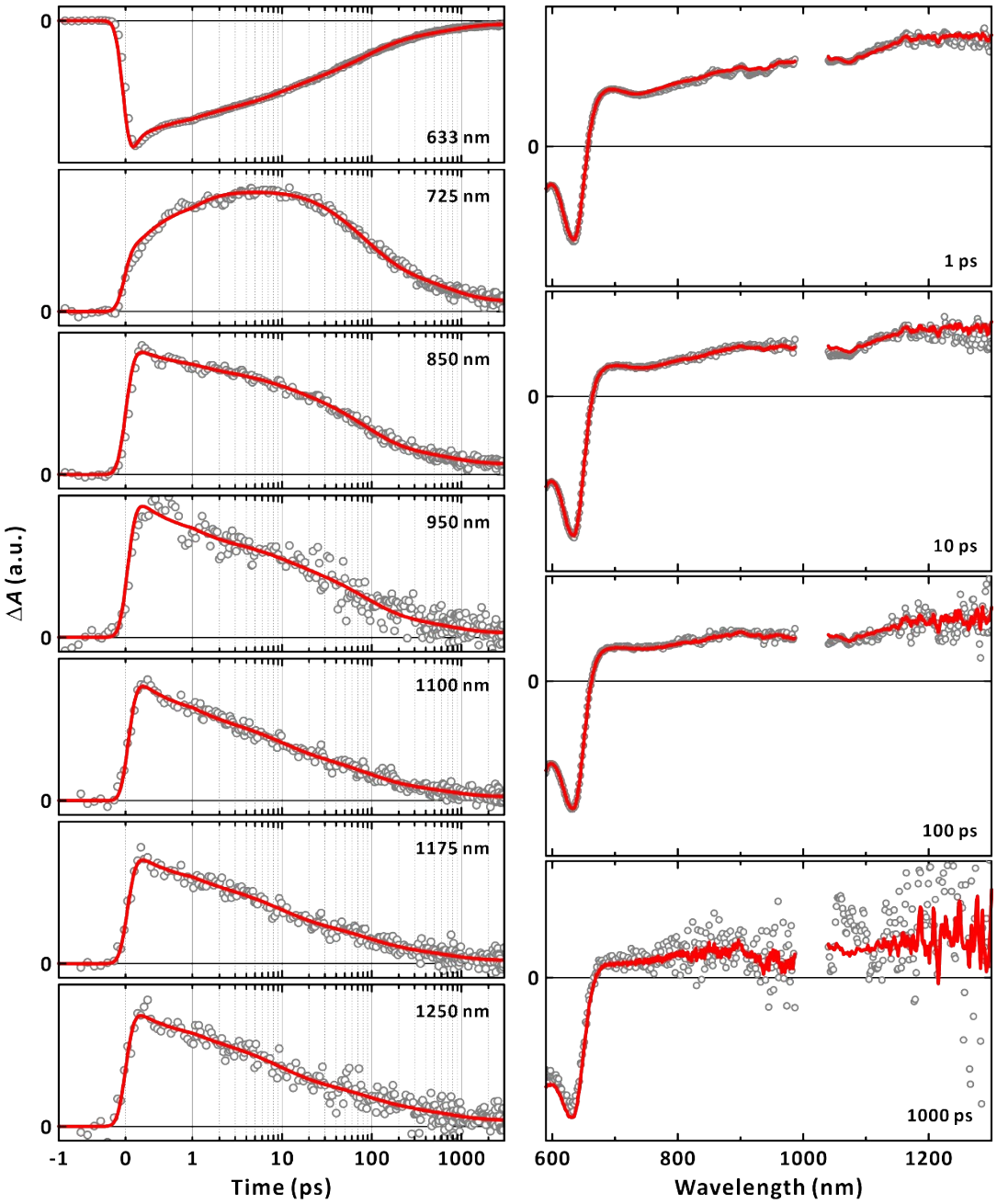

Fig. S4. Quality of global analysis. Kinetic profiles (left) and spectra (right) are presented with fit curves (solid lines) obtained from the global analysis in **Fig. 4(a)**. Representative wavelengths and time delays are given in the panels.

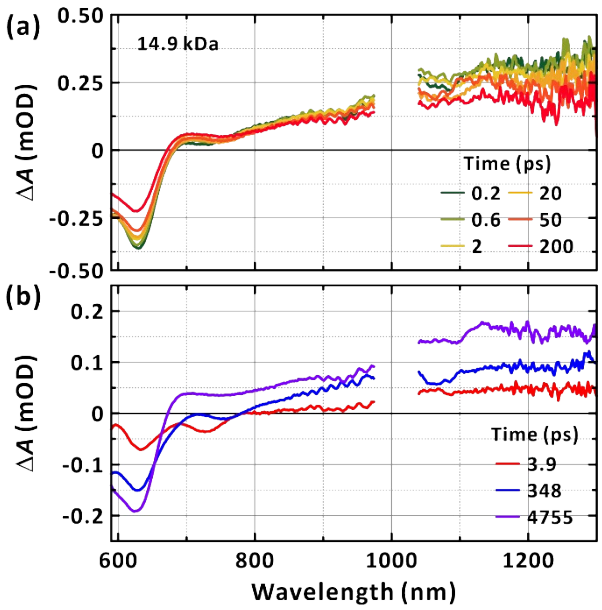

Fig. S5. TA spectroscopy of PM6 with M_n of 14.9 kDa. (a) TA spectra obtained with the excitation at 570 nm. [PM6] = 19 μg/mL. Representative time delays are given in the panel. (b) Lifetime-associated TA spectra. Global lifetime analysis was performed with three time constants. Time constants for the corresponding deconvoluted spectra are given in the panels.

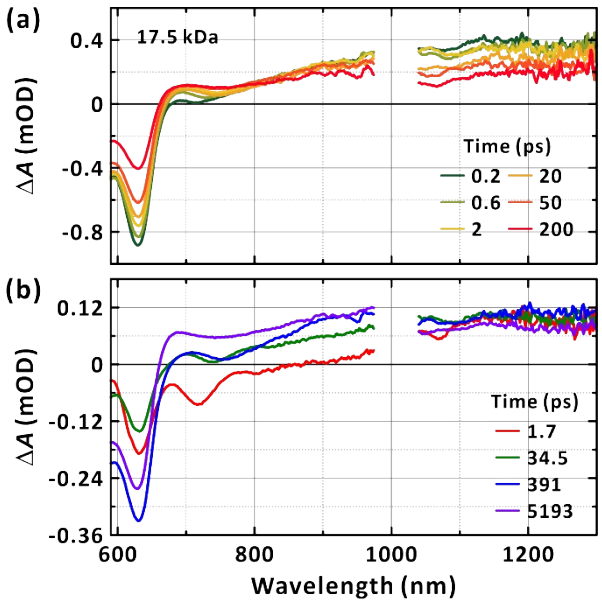

Fig. S6. TA spectroscopy of PM6 with M_n of 17.5 kDa. (a) TA spectra obtained with the excitation at 570 nm. [PM6] = 19 μg/mL. Representative time delays are given in the panel. (b) Lifetime-associated TA spectra. Global lifetime analysis was performed with four time constants. Time constants for the corresponding deconvoluted spectra are given in the panels.

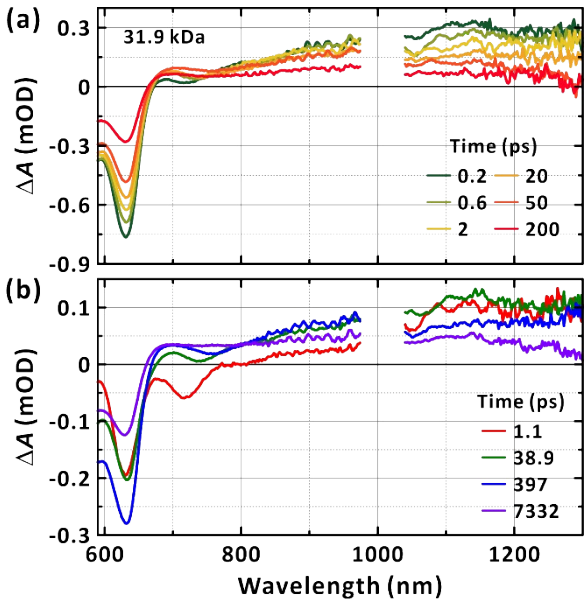

Fig. S7. TA spectroscopy of PM6 with M_n of 31.9 kDa. (a) TA spectra obtained with the excitation at 570 nm. [PM6] = 19 μg/mL. Representative time delays are given in the panel. (b) Lifetime-associated TA spectra. Global lifetime analysis was performed with four time constants. Time constants for the corresponding deconvoluted spectra are given in the panels.

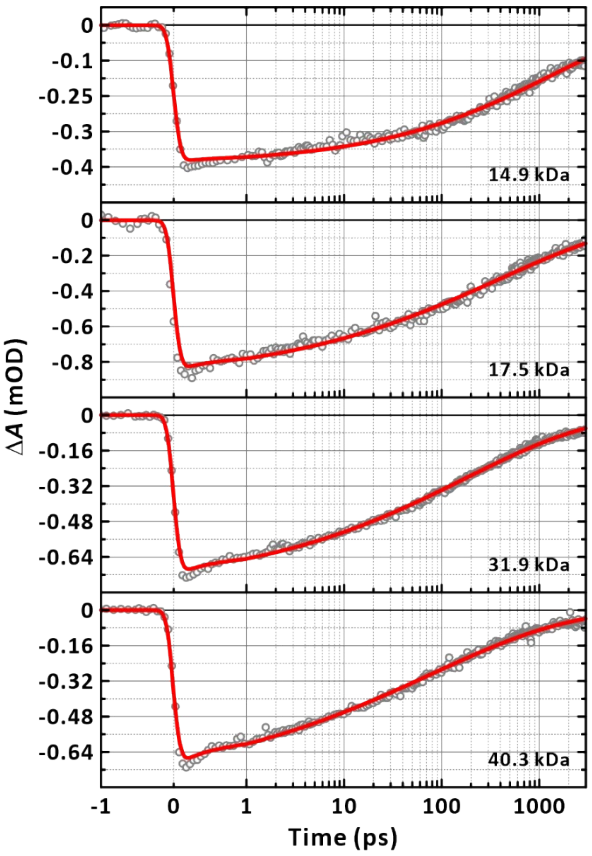

Fig. S8. Dependence of LE dynamics on chain-length without ultrafast component. Excitation and probed wavelengths are 570 nm and 635 nm, respectively. Number average molecular weights (M_n) of the samples are given in the panels. All transients are fitted to a stretched-exponential function, $\Delta A(t) = \Delta A_1 \exp[-(t/\tau_1)^{\beta}]$, convoluted with the Gaussian instrument response function. The fit curves are given in solid lines.

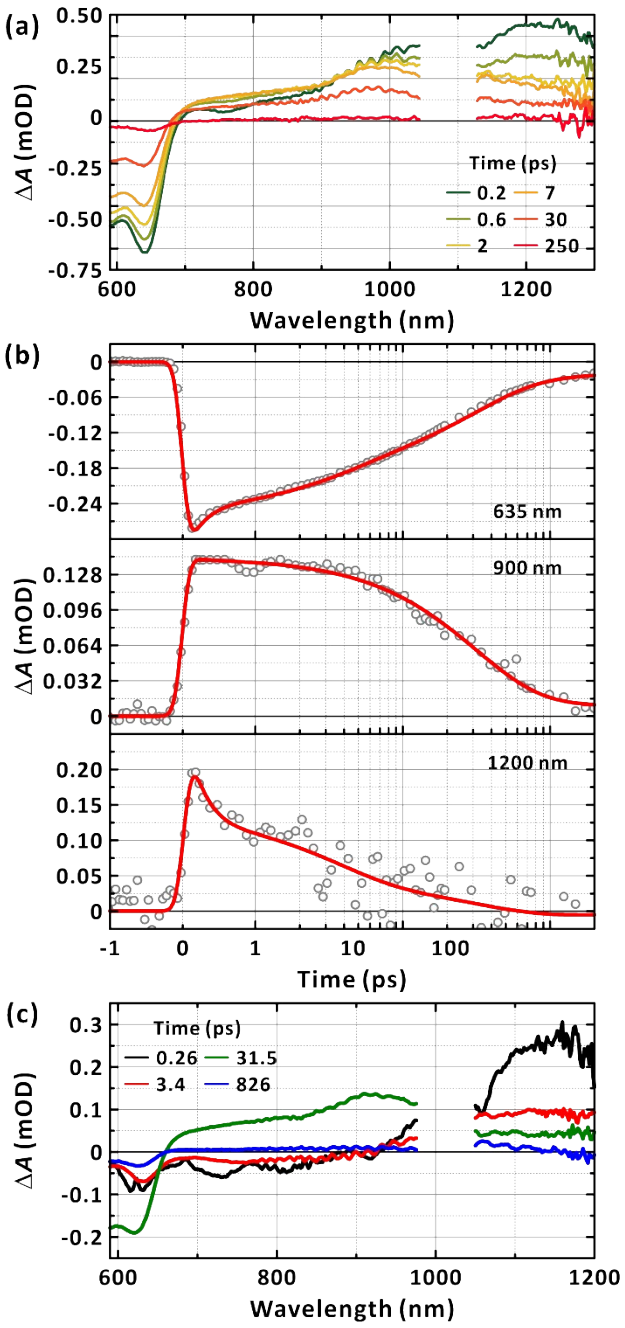

Fig. S9. Transient-absorption (TA) spectroscopy of spin-coated PM6 film. (a) TA spectra obtained with excitation at 570 nm. Representative time delays are given in the panel. (b) TA kinetic profiles. Probed wavelengths are given in the corresponding panels. Multi-exponential fits are also given in solid lines. (c) Lifetime-associated TA spectra. Global lifetime analysis

was performed with four time constants. Time constants for the corresponding deconvoluted spectra are given in the panel.