# **Supporting Information**

# Excited-State Dynamics of Pyrene Incorporated into Poly(substituted methylene)s: Effects of Dense Packing of Pyrenes on Excimer Formation

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#### **Experimental Section**

**Materials.** Tetrahydrofuran (THF, Junsei Chemical, >99.5%) was dried over Na/K alloy and distilled before use. Pyrene (Tokyo Chemical Industry, >98.0%), 2-chloro-2-methylpropane (Tokyo Chemical Industry, >98.0%), aluminum chloride(III) (Nacalai Tesque, >98%), bromine (Wako Pure Chemical Industries, >99.0%), *n*-butyllithium (Kanto Chemical, 1.63 M in hexane), trimethyl borate (Tokyo Chemical Industry, >97%), acetic acid (Kanto Chemical, >99.5%), hydrogen peroxide (Nacalai Tesque, 30% in H<sub>2</sub>O), bromoacetyl bromide (Tokyo Chemical Industry, >98.0%), NaHCO<sub>3</sub> (Wako Pure Chemical Industries, >99.0%), pyridine (Wako Pure Chemical Industry, >98.0%), acetic acid (Kanto Chemical, >99.5%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; Tokyo Chemical Industry, >98.0%), acryloyl chloride (Tokyo Chemical Industry, >98.0%), triethylamine (Nacalai Tesque, >99.0%), 1,1'-azobis(cyclohexane-1-carbonitrile) (Wako Pure Chemical Industries, >95.0%), potassium hydroxide (Nacalai Tesque, >85.0%), CaH<sub>2</sub> (Nacalai Tesque, >99.0%), Na<sub>2</sub>SO<sub>4</sub> (Nacalai Tesque, >98.5%), MgSO<sub>4</sub> (Wako Pure Chemical Industries, >98.0%), allylpalladium(II) chloride dimer ( $\pi$ -allylPdCl; Sigma-Aldrich, >98%), and sodium tetraphenylborate (NaBPh<sub>4</sub>; Kanto Chemical, >99.5%) were used as received. 1-Bromo-7-*tert*-butylpyrene [1], *N*,*N*'-ditosylhydrazine [2], 7-*tert*-butyl-1-pyrenemethanol [3], and 1-pyrenebutanol [4] were prepared according to the literatures. *Caution!* Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

#### Monomer Synthesis.

Synthesis of 7-tert-butylpyrenyl diazoacetate (monomer for poly1) [2]

Under a N<sub>2</sub> atmosphere, a THF (6 mL) solution of *n*-butyllithium (1.1 mL, 1.8 mmol) was placed in a round bottomed flask, and cooled to -78 °C. A THF (6 mL) solution of 1-bromo-7-*tert*-butylpyrene (0.20 g, 0.59 mmol) was added dropwise to the solution, and the mixture was stirred at -78 °C for 1 h. After trimethyl borate (0.36 mL, 3.2 mmol) was added dropwise to the solution, the mixture was stirred for 1 h and warmed to room temperature. Acetic acid (0.34 mL, 5.9 mmol) and hydrogen peroxide (0.32 mL, 3.1 mmol) were added and the mixture was stirred at room temperature for 30 min. CHCl<sub>3</sub> was added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of the solvent under reduced pressure, the residue was purified with silica gel short column (eluent: CH<sub>2</sub>Cl<sub>2</sub>) and preparative recycling size-exclusion chromatography (SEC) (eluent: CHCl<sub>3</sub>) to give 0.10 g (0.36 mmol, 61%) of 7-*tert*-butyl-1-pyrenol. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 10.55 (br-s, 1H, -OH), 8.32-8.28 (m, 1H, Ar–*H*), 8.16 (s, 2H, Ar–*H*), 8.08-7.94 (m, 3H, Ar–*H*), 7.89-7.85 (m, 1H, Ar–*H*), 7.58-7.54 (m, 1H, Ar–*H*), 1.51 (s, 9H, -C[CH<sub>3</sub>]<sub>3</sub>).

Under a N<sub>2</sub> atmosphere, an acetonitrile (10 mL) solution of 7-*tert*-butyl-1-pyrenol (0.40 g, 1.5 mmol) and pyridine (0.25 mL, 3.1 mmol) was placed in a round bottomed flask, and cooled to 0 °C. Bromoacetyl bromide (0.20 mL, 2.3 mmol) was added dropwise to the suspension at 0 °C, and the mixture was stirred at the temperature for 10 min. Water and CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure.

After *N*,*N*'-ditosylhydrazine (1.0 g, 2.9 mmol) was added to the residue under a N<sub>2</sub> atmosphere, THF (10 mL) was added to form a solution, which was cooled to 0 °C. DBU (1.1 mL, 7.8 mmol) was added to the solution, which was then stirred at 0 °C for 10 min. The mixture was transferred to a separatory funnel with Et<sub>2</sub>O and water. The separated organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with silica gel short column (eluent: CH<sub>2</sub>Cl<sub>2</sub>) and preparative recycling SEC (eluent: CHCl<sub>3</sub>) to give 0.31 g (0.91 mmol, 61%) of 7-*tert*-butylpyrenyl diazoacetate as pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.18 (s, 2H, Ar–*H*), 8.06-8.00 (m, 3H, Ar–*H*), 7.97-7.91 (m, 2H, Ar–*H*), 7.76-7.72 (m, 1H, Ar–*H*), 5.09 (br-s, 1H, N<sub>2</sub>=C*H*–), 1.54 (s, 9H, –C[CH<sub>3</sub>]<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 149.6, 144.0, 131.0, 130.9, 129.2, 128.5, 127.4, 127.0, 125.6, 124.9, 123.2, 122.9, 122.8, 122.6, 120.1, 119.5, 47.0 (br), 35.3, 32.0. The signal for the carbonyl carbon atom cannot be identified, probably because of its broadness. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.91; H, 5.33; N, 7.98.

#### Synthesis of 7-*tert*-butyl-1-pyrenylmethyl diazoacetate (monomer for poly2)

Under a N<sub>2</sub> atmosphere, a DMF (10 mL) solution of 7-*tert*-butyl-1-pyrenemethanol (0.41 g, 1.4 mmol) and pyridine (0.23 mL, 2.9 mmol) was placed in a round bottomed flask, and cooled to 0 °C. Bromoacetyl bromide (0.18 mL, 2.2 mmol) was added dropwise to the suspension at 0 °C, and the mixture was stirred at the temperature for 10 min. Water and CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. After *N*,*N*'-ditosylhydrazine (0.95 g, 2.9 mmol) was added to the residue under a N<sub>2</sub> atmosphere, THF (10 mL) was added to form a solution, which was cooled to 0 °C. DBU (0.99 mL, 7.1 mmol) was added to the solution, which was then stirred at 0 °C for 10 min. The mixture was transferred to a separatory funnel with Et<sub>2</sub>O and water. The separated organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with SEC (eluent: CHCl<sub>3</sub>) to give 0.31 mg (0.87 mmol, 62%) of 7-*tert*-butyl-1-pyrenylmethyl diazoacetate as pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.31-8.29 (m, 2H, Ar–*H*), 8.24-8.21 (m, 1H, Ar–*H*), 8.15-8.12 (m, 1H, Ar–*H*), 8.00-7.97 (m, 2H, Ar–*H*), 5.90 (s, 1H, –*CH*2–), 4.80 (s, 1H, N<sub>2</sub>=*CH*–), 1.68 (s, 9H, –C[CH<sub>3</sub>]<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 166.9 (br), 149.2, 131.6, 131.1, 130. 6, 129.3, 128.5, 128.4, 128.0, 127.3, 127.2, 124.7, 124.4, 122.8, 122.7 (d), 65.0, 46.4, 35.3, 32.0. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.00; H, 5.59; N, 6.95.

#### Synthesis of 4- pyrenyl-*n*-butyl diazoacetate (monomer for poly**3**)

Under a N<sub>2</sub> atmosphere, an acetonitrile (15 mL) suspension of 1-pyrenebutanol (0.79 g, 2.9 mmol) and NaHCO<sub>3</sub> (0.73 g, 8.7 mmol) was placed in a round bottomed flask, and cooled to 0 °C. Bromoacetyl bromide (0.35 mL, 4.1 mmol) was added dropwise to the suspension at 0 °C, and the mixture was stirred at the temperature for 10 min. Water and CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. After *N*,*N*'-ditosylhydrazine (1.9 g, 5.5 mmol) was added to the residue under a N<sub>2</sub> atmosphere, THF (10 mL) was added to form a solution, which was cooled to 0 °C. DBU (1.9 mL, 14 mmol) was added to the solution, which was then stirred at 0 °C for 10 min. The mixture was transferred to a separatory funnel with Et<sub>2</sub>O and water. The

separated organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with silica gel short column (eluent: CH<sub>2</sub>Cl<sub>2</sub>) and preparative recycling SEC (eluent: CHCl<sub>3</sub>) to give 0.44 g (1.3 mmol, 45%) of 4- pyrenyl-*n*-butyl diazoacetate as pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.25-8.21 (m, 1H, Ar–*H*), 8.16-8.07 (m, 4H, Ar–*H*), 8.01-7.95 (m, 3H, Ar–*H*), 7.84-7.82 (m, 1H, Ar–*H*), 4.70 (s, 1H, N<sub>2</sub>=C*H*–), 4.22 (t, *J* = 6.4 Hz, 2H,  $-CO_2CH_2CH_2CH_2CH_2CH_2$ , 3.35 (t, *J* = 6.4 Hz, 2H,  $-CO_2CH_2CH_2CH_2$ , 1.93-1.78 (m, 4H,  $-CO_2CH_2CH_2CH_2CH_2$ ). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 166.9 (br), 136.3, 131.5, 130.9, 129.9, 128.6, 127.5, 127.3, 127.2, 126.7, 125.8, 125.1, 125.0, 124.9, 124.8, 124.7, 123.3, 64.7, 46.2, 33.0, 28.8, 28.0. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.57; H, 5.27; N, 8.15.

#### Synthesis of 7-tert-butylpyrenyl acrylate (monomer for poly1')

Under a N<sub>2</sub> atmosphere, a THF (7 mL) solution of 7-*tert*-butyl-1-pyrenol (0.99 g, 3.6 mmol) and triethylamine (0.75 mL, 5.6 mmol) was placed in a Schlenk tube, and cooled to 0 °C. Acryloyl chloride (0.44 mL, 5.4 mmol) was added dropwise to the mixture at 0 °C, and the resulting mixture was warmed and stirred at room temperature for 3.5 h. Water and CHCl<sub>3</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with preparative recycling SEC (eluent: CHCl<sub>3</sub>) to give 0.76 g (2.3 mmol, 64%) of 7-*tert*-butylpyrenyl acrylate as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.24-8.21 (m, 2H, Ar–*H*), 8.16-8.13 (m, 1H, Ar–*H*), 8.09-8.03 (m, 4H, Ar–*H*), 7.80-7.78 (m, 1H, Ar–*H*), 6.81 (d, *J* = 18.0 Hz, CH<sub>2</sub>=CH–), 6.57 (dd, *J* = 18.0 Hz, 10.4 Hz, CH<sub>2</sub>=CH–), 6.16 (d, *J* = 10.4 Hz, 1H, CH<sub>2</sub>=CH–), 1.58 (s, 9H, –C[CH<sub>3</sub>]<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$ ): 165.0, 149.4, 144.1, 133.1, 130.9, 129.2, 128.4, 127.9, 127.3, 126.9, 125.5, 124.8, 122.9, 122.8, 122.5, 120.1, 119.3, 35.3, 32.0. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: C, 84.12; H, 6.14. Found: C, 82.65; H, 6.13.

## Synthesis of 7-*tert*-butylpyrenyl acrylate (monomer for poly2')

Under a N<sub>2</sub> atmosphere, a THF (11 mL) solution of 7-*tert*-butyl-1-pyrenemethanol (1.47 g, 5.08 mmol) and triethylamine (1.1 mL, 7.6 mmol) was placed in a Schlenk tube, and cooled to 0 °C. Acryloyl chloride (0.62 mL, 7.6 mmol) was added dropwise to the mixture at 0 °C, and the resulting mixture was warmed and stirred at room temperature for 3.5 h. Water and CHCl<sub>3</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with preparative recycling SEC (eluent: CHCl<sub>3</sub>) to give 0.82 g (2.5 mmol, 49%) of 7-*tert*-butylpyrenyl acrylate as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.36-8.34 (m, 2H, Ar–*H*), 8.25-8.22 (m, 1H, Ar–*H*), 8.14-8.11 (m, 1H, Ar–*H*), 8.07-7.95 (m, 4H, Ar–*H*), 6.63 (d, *J* = 17.5 Hz, CH<sub>2</sub>=CH–), 5.89 (d, *J* = 10.5 Hz, 1H, CH<sub>2</sub>=CH–), 5.93 (s, 1H, –CH<sub>2</sub>–), 1.76 (s, 9H, –C[CH<sub>3</sub>]<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$ ): 166.0, 148.9, 131.3, 131.0, 130.9, 130.4, 129.0, 128.3, 128.1, 127.7, 127.0, 124.5, 124.2, 122.7, 122.6, 122.5, 64.6, 35.1, 31.9. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>: C, 84.18; H, 6.48. Found: C, 82.89; H, 6.54.

## Synthesis of 4- pyrenyl-*n*-butyl acrylate (monomer for poly**3'**)

Under a N2 atmosphere, a THF (11 mL) solution of 1-pyrenebutanol (0.78 g, 2.4 mmol) and triethylamine

(0.55 mL, 3.6 mmol) was placed in a Schlenk tube, and cooled to 0 °C. Acryloyl chloride (0.33 mL, 3.8 mmol) was added dropwise to the mixture at 0 °C, and the resulting mixture was warmed and stirred at room temperature for 3.5 h. Water and CHCl<sub>3</sub> were added and the mixture was transferred to a separatory funnel, with which the organic layer was separated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified with preparative recycling SEC (eluent: CHCl<sub>3</sub>) to give 0.36 g (1.1 mmol, 46%) of 4-pyrenyl-*n*-butyl acrylate as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.26-8.24 (m, 1H, Ar–*H*), 8.17-8.14 (m, 2H, Ar–*H*), 8.12-8.08 (m, 2H, Ar–*H*), 8.03-7.96 (m, 3H, Ar–*H*), 7.87-7.84 (m, 1H, Ar–*H*), 6.39 (d, *J* = 17.5 Hz, CH<sub>2</sub>=CH–), 6.11 (dd, *J* = 17.5 Hz, 10.5 Hz, CH<sub>2</sub>=CH–), 5.80 (d, *J* = 10.5 Hz, 1H, CH<sub>2</sub>=CH–), 4.23 (t, *J* = 6.5 Hz, 2H,  $-CO_2CH_2CH_2CH_2CH_2-$ ), 3.38 (t, *J* = 7.8 Hz, 2H,  $-CO_2CH_2CH_2CH_2-$ ), 1.97-1.83 (m, 4H,  $-CO_2CH_2CH_2CH_2CH_2-$ ). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$ ): 166.4, 136.3, 131.5, 131.0, 130.7, 129.9, 128.7, 128.6, 127.6, 127.3, 127.2, 126.7, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 123.3, 64. 5, 33.1, 28.7, 28.1. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: C, 84.12; H, 6.14. Found: C, 83.66; H, 6.14.

**Characterization.** The number-average molecular weight ( $M_n$ ) and polydispersity ratio [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] were measured by means of SEC on a Jasco-ChromNAV system equipped with a differential refractometer detector using THF as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with 6 poly(methyl methacrylate) standards (Shodex M-75;  $M_p$  = 2400-212000,  $M_w/M_n < 1.1$ ) and dibutyl sebacate (molecular weight = 314.5). The columns used for the SEC analyses was a combination of Styragel HR4 and HR2 (Waters; exclusion limit molecular weight = 600k and 20k for polystyrene, respectively; column size = 300 mm × 7.8 mm i.d.; average particle size = 5 µm). Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H and a JAIGEL-2H (Japan Analytical Industry; exclusion limit molecular weight = 70k and 5k for polystyrene, respectively; column size = 600 mm × 20 mm i.d.) using CHCl<sub>3</sub> as eluent at a flow rate of 3.8 mL/min at room temperature. NMR spectra were recorded on a Bruker Avance 400 (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) or Avance 500 (500 MHz for <sup>1</sup>H and 126 MHz for <sup>13</sup>C) spectrometer at room temperature (monomers) or at 50 °C (polymers). Elemental analyses were performed on a YANAKO CHN Corder MT-5.



Fig. S1 <sup>1</sup>H NMR spectra of (a) poly1 ( $M_n = 8100$ ,  $M_w/M_n = 1.47$ ), (b) poly2 ( $M_n = 10900$ ,  $M_w/M_n = 1.63$ ), (c) poly3 ( $M_n = 12800$ ,  $M_w/M_n = 1.69$ ), (d) poly1' ( $M_n = 8500$ ,  $M_w/M_n = 1.20$ ), (e) poly2' ( $M_n = 8300$ ,  $M_w/M_n = 1.17$ ), and (f) poly3' ( $M_n = 7900$ ,  $M_w/M_n = 1.31$ ).



**Fig. S2** Absorption spectra of THF solutions of (a) poly1 and (b) its monomer, (c) poly2 and (d) its monomer, and (e) poly3 and (f) its monomer  $(13 \ \mu g/mL)$ .



**Fig. S3** Absorption spectra of THF solutions of (a) poly1' and (b) its monomer, (c) poly2' and (d) its monomer, and (e) poly3' and (f) its monomer (13  $\mu$ g/mL).



**Fig. S4** Fluorescence spectra of THF solutions of monomers for (a) poly1, (b) poly1', (c) poly2, (d) poly2', (e) poly3, and (f) poly3' (1.3 μg/mL).



**Fig. S5** The picosecond time-resolved fluorescence lifetimes of poly1 (a), poly2 (b), poly3 (c) and poly1' (d), poly2' (e), poly3' (f) in THF with photoexcitation at 377 nm. Black and red colors indicate results at the monitoring wavelength of 440 nm and 480 nm (460 nm for poly1, and poly1'), respectively.

# Femtosecond Time-resolved Near-IR Absorption Spectra of Pyrenyl Alcohols and Poly(1pyrenylalkylacrylate)s.

Femtosecond time-resolved near-IR absorption spectra of pyrenyl alcohols, **2** and **3**, and poly(1-pyrenylalkylacrylate)s, poly**2'** and poly**3'**, were recorded for investigating the effects of dense substitution. The results are shown in Figs. S6 and S7.



**Fig. S6** The femtosecond time-resolved near-IR absorption spectra of poly2' (a) and the transient near-IR absorption spectrum of 2 at 1 ns (b) in dichloromethane with photoexcitation at 345 nm.



**Fig. S7** The femtosecond time-resolved near-IR absorption spectra of poly3' (a) and the transient near-IR absorption spectrum of 3 at 1 ns (b) in dichloromethane with photoexcitation at 345 nm.

#### **Global Least-Squares Fitting Analysis.**

As mentioned in the main text, the time evolutions of the absorbance changes were simultaneously analyzed at every 10 nm from 910 to 1410 nm with the sum of exponential functions with common time constants,

$$A(\lambda,t) = \sum_{i} A_{i}(\lambda) e^{-\frac{t}{T_{i}}},$$
(S1)

where  $A_i(\lambda)$  and  $T_i$  represent the amplitude and time constant of the *i*-th exponential function, respectively. The  $A_i(\lambda)$  values plotted against wavelength, or the decay-associated spectra, are shown in Fig. S8. The positive and negative  $A_i(\lambda)$  values indicate the decay and the rise of transient absorption, respectively, with the time constant of  $T_i$ . For all the polymers, the spectral component associated with the slowest time constant of >1 ns,  $A_0(\lambda)$ , takes positive values in the entire wavelength range of our spectrometer. The  $A_0(\lambda)$  component, therefore, indicates the decay of the pyrene excimer with a time constant longer than the measurable time range of our spectrometer, 1 ns. The  $A_1(\lambda)$  component takes negative values in the entire wavelength range, indicating a rise of absorption with a time constant of  $T_1$ . When the sign of  $A_1(\lambda)$  is inverted, the shape of the  $A_1(\lambda)$  component agree well with that of the  $A_0(\lambda)$ component in the 1200–1400 nm region, where the pyrene excimer predominantly shows its absorption band. In addition, the difference spectrum between  $A_0(\lambda)$  and  $-A_1(\lambda)$  agrees well with the monomer absorption band except for poly3' (Fig. S9). From these agreements in the shape, the  $A_1(\lambda)$  component is assigned to the excimer formation process. Since the origin of the  $A_1(\lambda)$  component is explained well by only the decay of the monomer absorption and the rise of the excimer absorption, no intermediate is present in the excimer formation process (Scheme S1a). The monomer absorption bands of pyreneincorporated poly(substituted methylene)s retrieved from the decay-associated spectra show much larger widths of the sub-peaks than those of pyrene-incorporated polyacrylates (Fig. S9). The decayassociated spectra support stronger electronic interaction of the pyrene rings in pyrene-incorporated poly(substituted methylene)s.

As shown in Fig. S8, poly2, poly3, and poly3' exhibit two rise components with amplitudes of  $A_1(\lambda)$  and  $A_2(\lambda)$ . The  $A_1(\lambda)$  and  $A_2(\lambda)$  components are similar to each other in the wavelength range where the excimer absorption band appears, while they show substantial differences in the monomer absorption band. For poly2 and poly3, the  $A_1(\lambda)$  component shows larger widths of the sub-peaks than the  $A_2(\lambda)$  component in the monomer absorption band (Fig. S9). The difference indicates the presence of two different environments for pyrene in poly(substituted methylene)s, where a pyrene ring can either

strongly  $(A_1(\lambda))$  or weakly  $(A_2(\lambda))$  interact with its adjacent rings (Scheme S1b). The two environments will stay unchanged in the time scale of the excimer formation, because both the  $A_1(\lambda)$  and  $A_2(\lambda)$ components show an increase of the excimer absorption. While both the  $A_1(\lambda)$  and  $A_2(\lambda)$  components of poly2 and poly3 clearly show decays of the excited monomer, the  $A_1(\lambda)$  component of poly3' shows a complex shape in the wavelength range of the monomer absorption. The shape of the  $A_1(\lambda)$  component possibly suggests that another photophysical process exists in the picosecond regime for poly3' but the process is not separately observed within the sensitivity of our spectrometer.



**Fig. S8** Decay-associated absorption spectra of poly1 (a), poly1' (b), poly2 (c), poly2' (d), poly3 (e) and poly3' (f) in dichloromethane obtained by the global least-squares fitting analysis. The time constants were separately estimated by the least-squares fitting analysis at the absorption maximum wavelength of the excimer.



Fig. S9 Difference spectra between the decay-associated spectrum with a lifetime of >1 ns  $(A_0(\lambda))$  and the spectrum with a rise in the picosecond region  $(A_1(\lambda) \text{ or } A_2(\lambda))$  calculated for poly1 (a), poly1' (b), poly2 (c), poly2' (d), poly3 (e) and poly3' (f). The decay-associated spectra are arbitrarily scaled before calculation of the difference spectra so that the excimer absorption band fully disappears.



Scheme S1 The model of the excimer formation kinetics suggested by the global least-squares fitting analysis for poly1, poly1' and poly2' (a) and for poly2, poly3 and poly3' (b). The characters in (a), G, M and E, denote the ground state, the monomer excited state, and the excimer state, respectively. The characters in (b), G, M1, M2 and E, denote the ground state, the two monomer excited states in different environment, and the excimer state, respectively. The values  $k_1$ ,  $k_2$  and  $k_0$  represents the rate constants.

#### Estimation of Ratio of Excited Pyrene Monomers in Two Different Environments.

The global least-squares fitting analysis of the femtosecond time-resolved near-IR absorption spectra of poly2, poly3 and poly3' strongly suggests the presence of two different environment for excited pyrene monomers. We estimated the fractions of excited pyrene monomers in the two environments by assuming the kinetic model shown in Scheme 1b in the main text. The direct decay of the excited monomers to the ground state can be neglected, because the absorbance changes by the direct decay process are not retrieved well by the global least-squares fitting analysis.

When the excimer formation proceeds as shown in Scheme 1b, the rate equations to solve for M1, M2 and E are

$$\frac{d[M1](t)}{dt} = -\frac{1}{T_1}[M1](t),$$
(S2)

$$\frac{d[M2](t)}{dt} = -\frac{1}{T_2}[M2](t),$$
(S3)

$$\frac{d[E](t)}{dt} = \frac{1}{T_1} [M1](t) + \frac{1}{T_2} [M2](t) - \frac{1}{T_0} [E](t).$$
(S4)

Here  $T_1$ ,  $T_2$  and  $T_0$  are the time constants of the reactions. The solutions of the equations (S2), (S3) and (S4) are expressed as follows under the condition [E](0) = 0:

$$[M1](t) = [M1]^0 e^{-\frac{t}{T_1}},$$
(S5)

$$[M2](t) = [M2]^0 e^{-\frac{t}{T_2}},$$
(S6)

$$[E](t) = \frac{T_0[M1]^0}{T_0 - T_1} \left( e^{-\frac{t}{T_0}} - e^{-\frac{t}{T_1}} \right) + \frac{T_0[M2]^0}{T_0 - T_2} \left( e^{-\frac{t}{T_0}} - e^{-\frac{t}{T_2}} \right).$$
(S7)

According to the Lambert-Beer law, the absorbance changes of the two monomers in different environments,  $A_{M1}(\lambda, t)$  and  $A_{M2}(\lambda, t)$ , and those of the excimer,  $A_E(\lambda, t)$ , are written as follows:

$$A_{\rm M1}(\lambda,t) = L\varepsilon_{\rm M1}(\lambda)[{\rm M1}](t) = L\varepsilon_{\rm M1}(\lambda)[{\rm M1}]^0 e^{-\frac{t}{T_1}} = A_{\rm M1}^0(\lambda)e^{-\frac{t}{T_1}},$$
 (S8)

$$A_{M2}(\lambda, t) = A_{M2}^{0}(\lambda)e^{-\frac{t}{T_{1}}},$$
(S9)

$$A_{\rm E}(\lambda,t) = A_{\rm E1}^0(\lambda)(e^{-\frac{t}{T_0}} - e^{-\frac{t}{T_1}}) + A_{\rm E2}^0(\lambda)(e^{-\frac{t}{T_0}} - e^{-\frac{t}{T_2}}),$$
(S10)

where

$$A_{\rm M1}^0(\lambda) = L\varepsilon_{\rm M1}(\lambda)[{\rm M1}]^0, \tag{S11}$$

$$A_{M2}^{0}(\lambda) = L\varepsilon_{M1}(\lambda)[M2]^{0}, \qquad (S12)$$

$$A_{\rm E1}^{0}(\lambda) = \frac{T_0 L \varepsilon_{\rm E}(\lambda) [\rm M1]^0}{T_0 - T_1},$$
(S13)

$$A_{\rm E2}^{0}(\lambda) = \frac{T_0 L \varepsilon_{\rm E}(\lambda) [\rm M2]^0}{T_0 - T_2}.$$
 (S14)

Here,  $\varepsilon_{M1}(\lambda)$ ,  $\varepsilon_{M2}(\lambda)$ , and  $\varepsilon_{E}(\lambda)$  are the molar extinction coefficients of the monomers in the two different environments and the excimer at the wavelength,  $\lambda$ , respectively, and *L* is the optical path length of the sample. The observed absorbance changes are given by the sum of the equations (S8), (S9) and (S10) as

$$A_{\text{obs}}(\lambda, t) = A_{\text{M1}}(\lambda, t) + A_{\text{M2}}(\lambda, t) + A_{\text{E}}(\lambda, t)$$
  
=  $[A_{\text{E1}}^{0}(\lambda) + A_{\text{E2}}^{0}(\lambda)]e^{-\frac{t}{T_{0}}}$   
+  $[A_{\text{M1}}^{0}(\lambda) - A_{\text{E1}}^{0}(\lambda)]e^{-\frac{t}{T_{1}}} + [A_{\text{M2}}^{0}(\lambda) - A_{\text{E2}}^{0}(\lambda)]e^{-\frac{t}{T_{2}}}.$  (S15)

When the following equation,

$$A_{\rm fit}(\lambda,t) = A_0(\lambda)e^{-\frac{t}{T_0}} + A_1(\lambda)e^{-\frac{t}{T_1}} + A_2(\lambda)e^{-\frac{t}{T_2}},$$
 (S16)

is used for the least-squares fitting analysis, the fitting parameters  $A_0$ ,  $A_1$  and  $A_2$  are related to the initial absorbance changes derived from the kinetic model by the following equations,

$$A_0(\lambda) = A_{\rm E1}^0(\lambda) + A_{\rm E2}^0(\lambda), \tag{S17}$$

$$A_{\rm I}(\lambda) = A_{\rm MI}^0(\lambda) - A_{\rm EI}^0(\lambda), \tag{S18}$$

$$A_2(\lambda) = A_{\rm M2}^0(\lambda) - A_{\rm E2}^0(\lambda). \tag{S19}$$

We define the value  $r_1(\lambda)$  as

$$r_1(\lambda) \equiv \frac{A_1(\lambda)}{A_1(\lambda) + A_2(\lambda)}.$$
(S20)

The results of the time-resolved near-IR absorption measurements clearly show that the time constants of the excimer formation are much smaller than that of the decay of the excimer. Provided that the time constants  $T_0$ ,  $T_1$ , and  $T_2$  satisfy the relations  $T_0 >> T_1$  and  $T_0 >> T_2$  and the molar extinction coefficients at the absorption maximum wavelength of the excimer  $\lambda_E^{max}$  satisfy the relation  $\varepsilon_{M1}(\lambda_E^{max}) \ll \varepsilon_E(\lambda_E^{max})$  and  $\varepsilon_{M2}(\lambda_E^{max}) \ll \varepsilon_E(\lambda_E^{max})$  to  $A_1(\lambda_E^{max})$  is rewritten using the equations (S11)–(S14), (S18) and (S19):

$$\frac{A_{2}(\lambda_{\rm E}^{\rm max})}{A_{1}(\lambda_{\rm E}^{\rm max})} = \left[ \varepsilon_{\rm M}(\lambda_{\rm E}^{\rm max}) - \frac{T_{0}\varepsilon_{\rm E}(\lambda_{\rm E}^{\rm max})}{T_{0} - T_{2}} \right] \left[ \varepsilon_{\rm M}(\lambda_{\rm E}^{\rm max}) - \frac{T_{0}\varepsilon_{\rm E}(\lambda_{\rm E}^{\rm max})}{T_{0} - T_{1}} \right]^{-1} \frac{[{\rm M2}]^{0}}{[{\rm M1}]^{0}}$$

$$\approx \varepsilon_{\rm E}(\lambda_{\rm E}^{\rm max}) [\varepsilon_{\rm E}(\lambda_{\rm E}^{\rm max})]^{-1} \frac{[{\rm M2}]^{0}}{[{\rm M1}]^{0}}$$

$$= \frac{[{\rm M2}]^{0}}{[{\rm M1}]^{0}}.$$
(S21)

The equation (S20) is written using the equation (S21) as

$$r_{1}(\lambda_{\rm E}^{\rm max}) = \frac{1}{1 + A_{2}(\lambda_{\rm E}^{\rm max})/A_{1}(\lambda_{\rm E}^{\rm max})} = \frac{[{\rm M1}]^{0}}{[{\rm M1}]^{0} + [{\rm M2}]^{0}}.$$
 (S22)

The equation (S22) shows that  $r_1(\lambda_E^{max})$  represents the fraction of excited pyrene monomers that undergo fast excimer formation. Similarly, the fraction of excited pyrene monomers that undergo slow excimer formation,  $r_2(\lambda_E^{max})$ , is defined and expressed as

$$r_{2}(\lambda_{\rm E}^{\rm max}) = \frac{A_{2}(\lambda_{\rm E}^{\rm max})/A_{1}(\lambda_{\rm E}^{\rm max})}{1 + A_{2}(\lambda_{\rm E}^{\rm max})/A_{1}(\lambda_{\rm E}^{\rm max})} = \frac{[{\rm M2}]^{0}}{[{\rm M1}]^{0} + [{\rm M2}]^{0}}.$$
(S23)

The obtained  $r_1(\lambda_E^{\text{max}})$  and  $r_2(\lambda_E^{\text{max}})$  values are shown in Table 2 in the main text for poly2, poly3 and poly3'.

## References

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