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*Electronic Supplementary Information*

# Structure-controlled polymers prepared by pseudo-living addition-condensation polymerization and their application to light harvesting

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## ***EXPERIMENTAL SECTION***

### ***Materials.***

Unless stated otherwise, reagents and solvents were purchased and used without purification. 1-

Methylpyrrole (Tokyo Kasei Chemical Co., Ltd., Tokyo, Japan) as a monomer was purified by distillation.

***Measurements.***

The UV-Vis spectra and fluorescence spectra were measured using a V-670 spectrophotometer and FP-8300 spectrophotometer (JASCO). $^1$H-NMR spectra were recorded on a JEOL ECS-400 spectrometer.

## 1 Normal and pseudo-living addition-condensation polymerizations of 1-methylpyrrole (MePyr) and aldehydes

### (a) Concept of reaction

### Step-1 Addition

In Figure S1a, the reaction starts by proton attack at the oxygen of the formyl group, generating a carbocation (Cation-A). Cation-A then attacks the α-position of MePyr because the electron density is higher at the α-position than the β-position. However, the reactivity of Cation-A is low because it has a hydroxyl group, which is an electron donating group. This lower reactivity leads to a high selectivity for the reaction.

### Step-2 Condensation

In Figure S1b, the MePyr-alcohol generated in Step-1 reacts with a proton, which allows water to leave, thus forming a new carbocation (Cation-C). Cation-C also attacks the α-position of MePyr and generates dipyrromethane. Here, the reactivity of Cation-C, which has no hydroxyl group, is much higher than that of Cation-A. Therefore, there is a lower selectivity for the reaction. This higher reactivity leads to a kinetic, rather than thermodynamic, driving force.

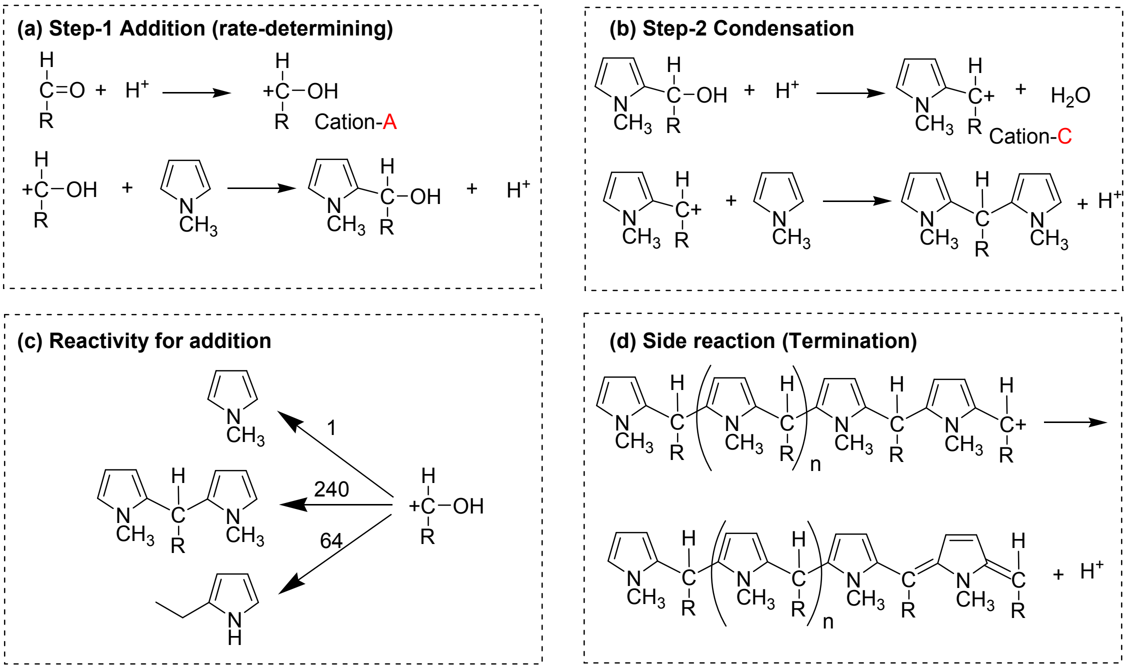


**Figure S1.** Basic addition-condensation polymerization of 1-methylpyrrole and aldehyde.

### (b) Reactivity ratios of dipyrromethane and 2-ethylpyrrole to MePyr in addition

### Normal

A solution of MePyr (5.00 mmol) and *p*-toluenesulfonic acid monohydrate (p-TS, 0.167 mmol) was prepared in dimethylformamide (DMF, 2.5 mL) and then mixed with another solution of 3-perylenecarboxaldehyde (PeA, 0.025 mmol, 2.5 mL DMF) at 10 °C. The reaction of PeA with MePyr was then spectroscopically monitored (Figure S2-1a). This reaction is pseudo-first order because of the excess amount of MePyr. The first order plot is shown in Figure S2-2. The rate constant estimated from the slope is $4.2 \times 10^{-5}$ $s^{-1}$.

### 1/1000 of the amount of dipyrromethane

MePyr (5.00 mmol), benzaldehyde-2-sulfonic acid sodium salt (BS, 0.005 mmol), and p-TS (0.167 mmol) were dissolved in DMF (2.5 mL) and kept at 10 °C for 30 min. NMR confirmed that no BS remained, indicating a complete conversion. A solution of PeA (0.025 mmol, 2.5 mL DMF) was added to the MePyr solution containing 1/1000 of the amount of dipyrromethane at 10 °C. The reaction of PeA with MePyr and 1/1000 of the amount of dipyrromethane was then monitored by spectroscopic measurement (Figure S2-1b), and the first order plot is shown in Figure S2-2a. The rate constant estimated from the slope is $5.2 \times 10^{-5}$ $s^{-1}$.

### 1/100 of the amount of 2-ethylpyrrole

MePyr (5.00 mmol), 2-ethylpyrrole (2-EtPyr, 0.05 mmol), and p-TS (0.167 mmol) were dissolved in DMF (2.5 mL). Another solution of PeA (0.025 mmol, 2.5 mL DMF) was added to the first solution at 10 °C. The reaction of PeA with MePyr and 1/100 of the amount of 2-EtPyr was then spectroscopically monitored (Figure S2-1c), and the first order plot is shown in Figure S2-2b. The rate constant estimated from the slope is $6.9 \times 10^{-5}$ $s^{-1}$.

**Reactivity ratio**

The rate constants for MePyr, dipyrromethane, and 2-EtPyr are represented as M, D, and E, respectively.

$M = 4.2 \times 10^{-5}\ s^{-1}$

From the 1/1000 of the amount of dipyrromethane system:

$0.998\ M + 1/1000\ D = 5.2 \times 10^{-5}\ s^{-1}$

Therefore, $D = 1.0 \times 10^{-2}\ s^{-1}$

The reactivity ratio of $D/M = 1.0 \times 10^{-2}\ s^{-1} / 4.2 \times 10^{-5}\ s^{-1} = 240$

From the 1/100 of the amount of 2-EtPyr system:

$M + 1/100\ E = 6.9 \times 10^{-5}\ s^{-1}$

Therefore, $E = 2.7 \times 10^{-3}\ s^{-1}$

The reactivity ratio of $E/M = 2.7 \times 10^{-3}\ s^{-1} / 4.2 \times 10^{-5}\ s^{-1} = 64$

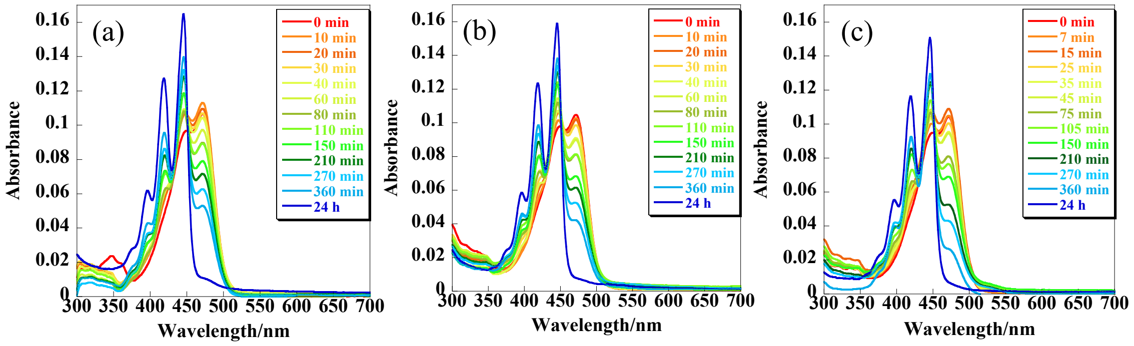
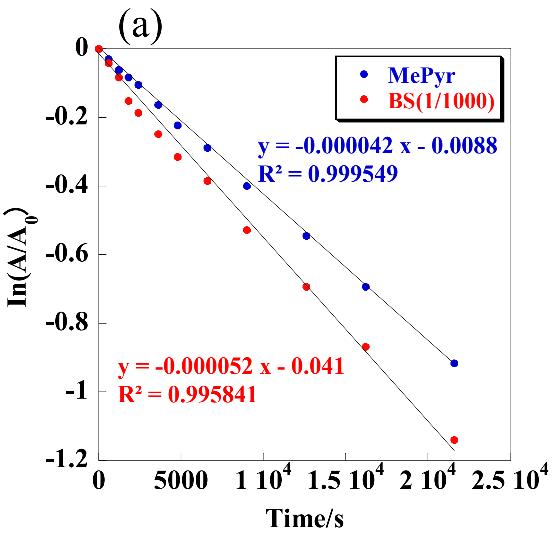
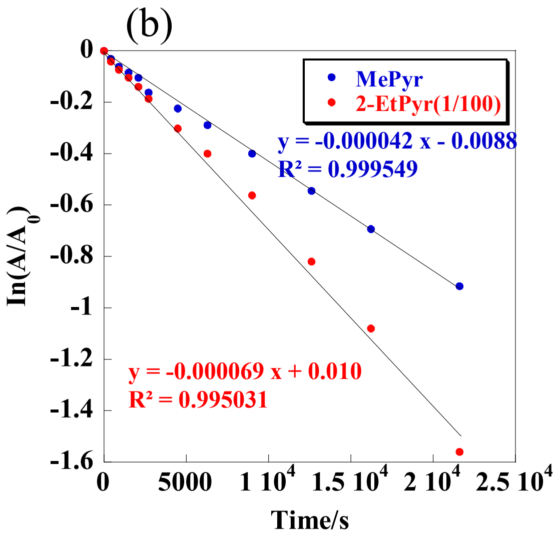


**Figure S2-1.** Absorption spectra at different reaction times for PeA (0.025 mmol) with (a) MePyr (5.00 mmol), (b) MePyr (5.00 mmol) and BS (0.005 mmol), and (c) MePyr (5.00 mmol) and 2-EtPyr (0.050 mmol) dissolved in DMF at 25 °C, cell length=1 cm.

**Figure S2-2.** First-order plots for the reaction of PeA (0.025 mmol) with MePyr (5.00 mmol) (a) in the presence and absence of BS (0.005 mmol); (b) in the presence and absence of 2-EtPyr (0.050 mmol).


(a)
MePyr
BS(1/1000)
y = -0.000042 x - 0.0088
R² = 0.999549
y = -0.000052 x - 0.041
R² = 0.995841
In(A/A0)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
5000
1 10^4
1.5 10^4
2 10^4
2.5 10^4
Time/s


(b)
MePyr
2-EtPyr(1/100)
y = -0.000042 x - 0.0088
R² = 0.999549
y = -0.000069 x + 0.010
R² = 0.995031
In(A/A0)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
0
5000
1 10^4
1.5 10^4
2 10^4
2.5 10^4
Time/s

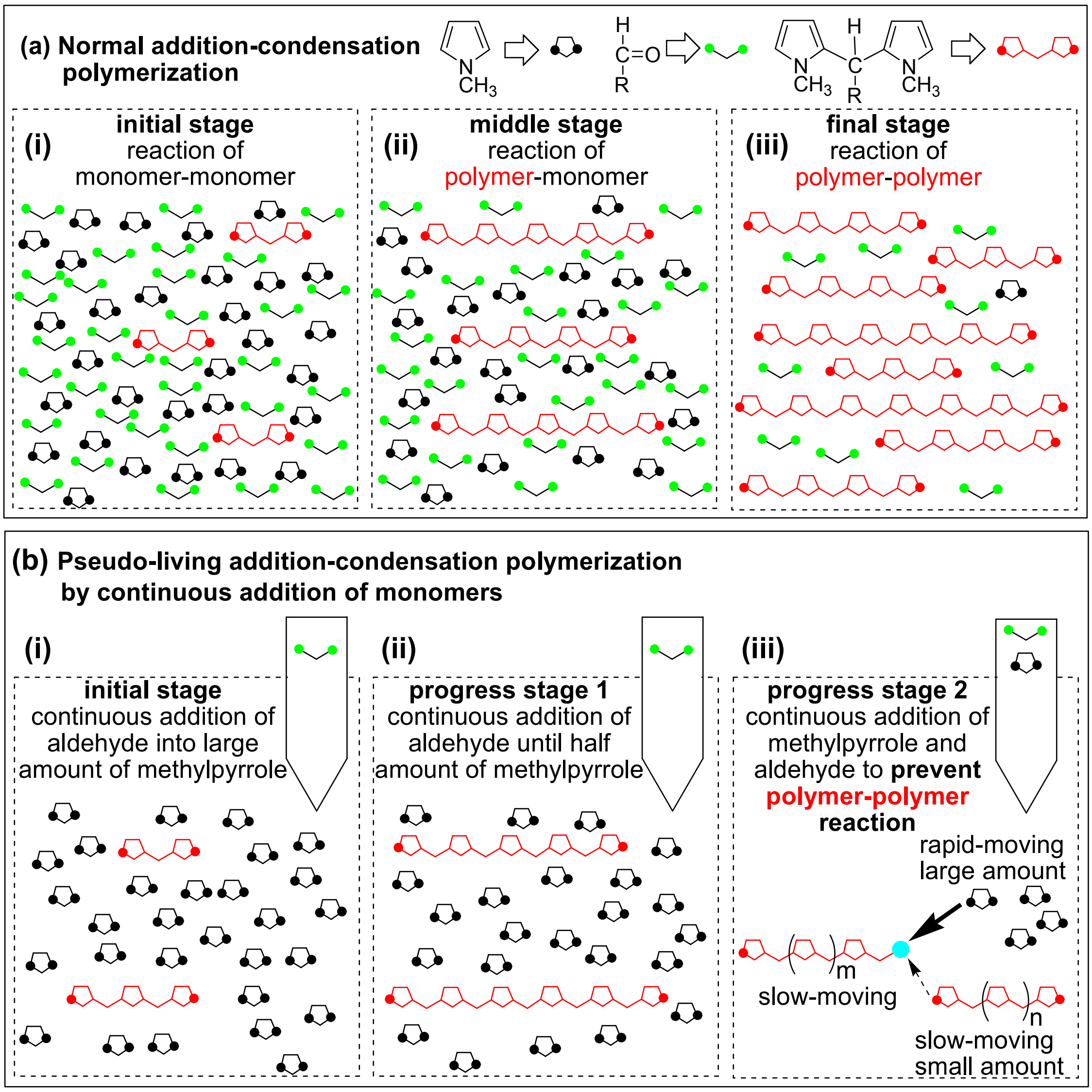


**Figure S3.** Image for the different reaction systems: (a) normal (b) pseudo-living addition-condensation polymerizations.

### (c) Polymerization data

**The polymerization of MePyr and equimolar BS:**

MePyr (36.0 mmol) and BS (36.0 mmol) were dissolved in DMF (18 mL). A second solution containing p-TS (1.20 mmol, 18 mL DMF) was added to this solution at 10 °C. The resulting solution was divided into 16 equal parts. After 5 min, a portion of the resulting solution was poured into isopropyl alcohol (45 mL) with potassium hydroxide (KOH, 0.90 mmol). The resulting precipitate was washed with isopropyl alcohol and lyophilized (yield: 0.171 g, 35.0%). Other polymers obtained at different times were similarly prepared.

The molecular weight was roughly determined by viscosity and NMR measurements. The number-average molecular weight was estimated by the signal intensity ratio of terminal α-proton and another proton attached to the benzene ring adjacent to the sulfo group (Figure S14). The Mark-Houwink-Sakurada formula was used to relate the viscosity and molecular weight:

$[\eta] = KM^{\alpha}$, $K = 1.21 \times 10^{-3}$, $\alpha = 0.464$.

Here, we used $[\eta]_{sp}/c$ at 0.40 g/dL instead of $[\eta]$ because $[\eta]_{sp}/c$ is almost constant at different concentrations.

Figure S4a shows the conversion-time curve. The conversion proceeded rapidly until 20 min (conversion of 67%), slowly increased from 20 to 60 min (conversion of 87%), and then became almost constant. Conversely, in the MW-conversion curve shown in Figure S4b, the MW gradually increased until 80% conversion was reached because the propagation reaction is very much like a chain-growth polymerization. Then the MW steeply increased at conversions above 80%, acting more like the step-growth polymerization of polyamide. Finally, the MW became constant because no further reactions occurred between the slow moving, high MW polymers.

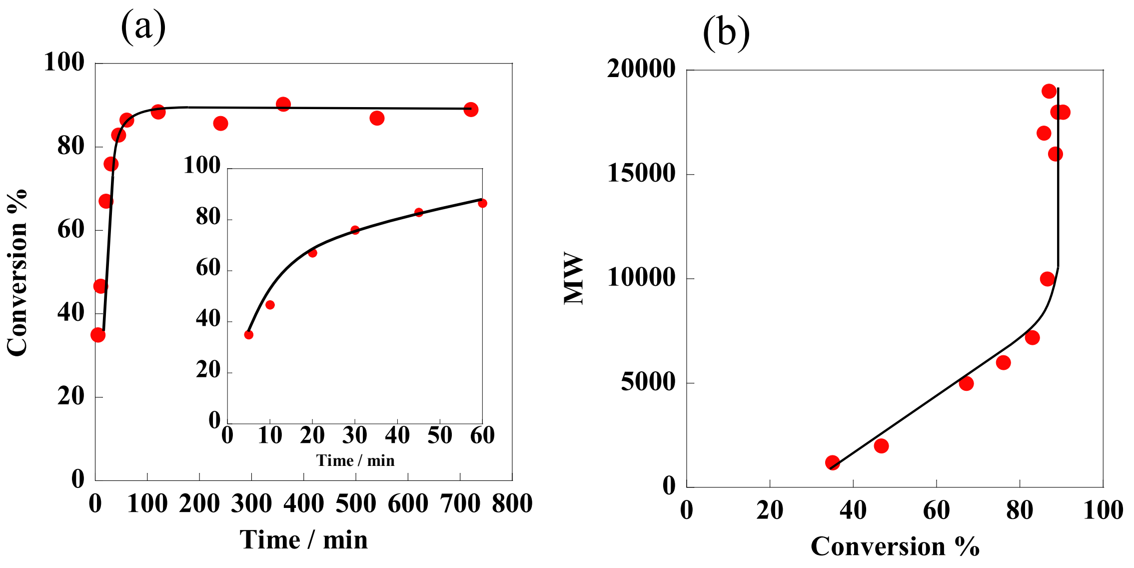


**Figure S4.** (a) Conversion-time curve and (b) MW-conversion curve of the polymerization of MePyr and BS.

## 2 Structure-controlled polymers prepared by pseudo-living addition-condensation

## polymerization by the continuous addition of monomers

### (a) The continuous-addition polymerization of MePyr with BS:

MePyr-BS (8 day) was prepared as follows:
Solution-A: MePyr (5.00 mmol), p-TS (0.167 mmol) in DMF (2.0 mL).
Solution-B: BS (2.5 mmol) in DMF (3.0 mL)
Solution-C: p-TS (1.33 mmol) in DMF (1.5 mL)
Solution-D: BS (17.5 mmol) and MePyr (17.5 mmol) in DMF (20 mL)

Solution-A was stirred (300 rpm) at 10 °C. Solution-B was continuously added to Solution-A for 24 h using a syringe driver (YSP-101, YMC Co., Ltd.). Then, Solution-C and Solution-D were simultaneously and continuously added for 168 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 3.2 mL) at 192 h. Isopropyl alcohol (240 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of DMF/isopropyl alcohol (48 mL/240 mL) and two times of water/isopropyl alcohol (36 mL/240 mL), and then dissolved in water. The polymer was obtained by freeze-drying (3.619 g, 66.7%). The other polymers were similarly prepared. The conversions and molecular weights of the obtained polymers are shown in Table S1.

The molecular-weight-distribution of the polymer obtained at 8 days was roughly estimated as follows: the MePyr-BS (8 day) polymer (1.00 g) was dissolved in water (8.0 mL), then the large polymer (0.276 g, 25.4%, MW = 90000 g/mol), middle polymer (0.293 g, 27.1%, MW = 42000 g/mol), and small polymer (0.252 g, 23.2%, Mw = 18000 g/mol) were obtained using 16.6, 24.4, and 33.3 mL of isopropyl alcohol, respectively.
The ratios for the polymer weights are: $w_L = 25.4/23.2 = 1.09$, $w_m = 27.1/23.2 = 1.17$, and $w_s = 1$.

$$\boldsymbol{Mn} = \frac{\Sigma\, \boldsymbol{Ni\ Mi}}{\Sigma\, \boldsymbol{Ni}} = \frac{\Sigma \frac{\boldsymbol{wi}}{\boldsymbol{Mi}} \boldsymbol{Mi}}{\Sigma \frac{\boldsymbol{wi}}{\boldsymbol{Mi}}} = \frac{\Sigma\, \boldsymbol{wi}}{\Sigma \frac{\boldsymbol{wi}}{\boldsymbol{Mi}}}$$

$$\boldsymbol{Mw} = \frac{\Sigma\, \boldsymbol{Ni\ Mi2}}{\Sigma\, \boldsymbol{Ni\ Mi}} = \frac{\Sigma \frac{\boldsymbol{wi}}{\boldsymbol{Mi}} \boldsymbol{Mi2}}{\Sigma\, \boldsymbol{wi}} = \frac{\Sigma\, \boldsymbol{wi\ Mi}}{\Sigma\, \boldsymbol{wi}}$$

$\mathbf{M_n}$ = (1.09 + 1.17 + 1) / [(1.09 / 90000) + (1.17 / 42000) + (1 / 18000)] = 34000
$\mathbf{M_w}$ = (1.09 × 90000 + 1.17 × 42000 + 1 × 18000) / (1.09 + 1.17 + 1) = 51000
$\mathbf{M_w / M_n}$ = 51000 / 34000 = 1.50

**Table S1.** Conversions and molecular weights of the polymers.

| | $[\eta]_{sp}$ / C | MW | Conversion % |
|---|---|---|---|
| 1 day | 0.07 | 6800 | 63.2 |
| 2 day | 0.10 | 15000 | 65.9 |
| 4 day | 0.13 | 25000 | 63.5 |
| 6 day | 0.15 | 37000 | 62.7 |
| 8 day | 0.18 | 53000 | 66.7 |

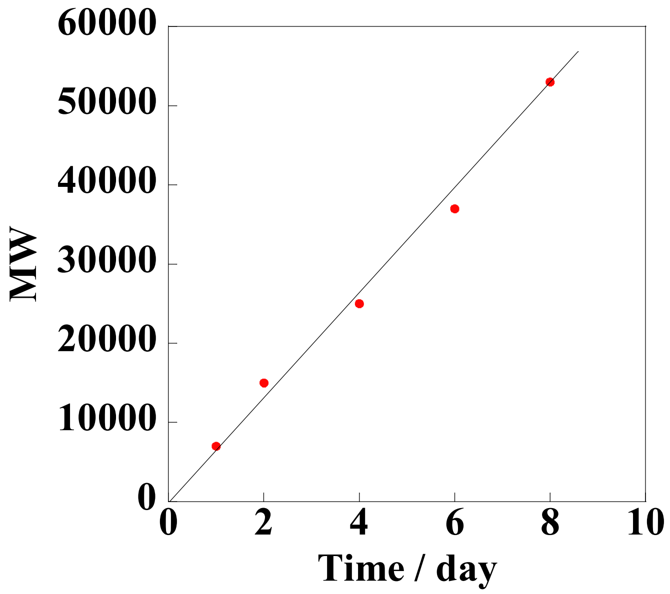


**Figure S5.** MW-time curve for the pseudo-living addition-condensation polymerization of MePyr and BS with the continuous addition of monomers.

### (b) A, B-block amphiphilic polymer for interphase photoinduced energy transfer

Figure S6 shows the schedule for preparing the A, B-block amphiphilic polymer by the continuous addition of the monomer.

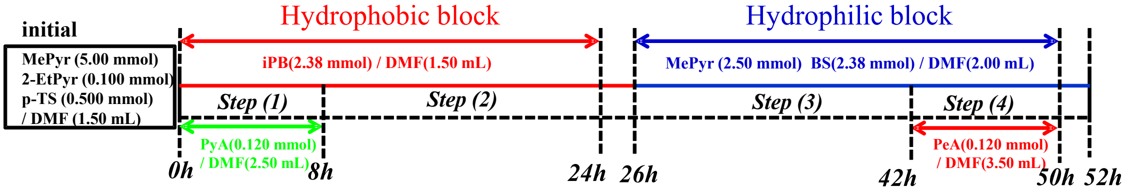


**Figure S6.** Schedule for the continuous addition polymerization of amphiphilic polymers.

**iPB(Py)-BS(Pe)** was prepared as follows:

Solution-E: MePyr (5.00 mmol), 2-EtPyr (0.10 mmol), p-TS (0.50 mmol) in DMF (1.5 mL).

Solution-F: 4-isopropylbenzaldehyde (iPB, 2.38 mmol) in DMF (1.5 mL)

Solution-G: 1-Pyrenecarboxaldehyde (PyA, 0.12 mmol) in DMF (2.5 mL)

Solution-H: BS (2.38 mmol) and MePyr (2.50 mmol) in DMF (2.0 mL)

Solution-I: 3-Perylenecarboxaldehyde (PeA, 0.12 mmol) in DMF (3.5 mL)

Solution-E was stirred (300 rpm) at 30 °C. Solution-F was continuously added to Solution-E for 24 h. At the same time, Solution-G was also continuously added for 8 h. At 26 h, the reaction system was cooled to 10 °C. Solution-H was continuously added for 24 h. Then, at 42 h, Solution-I was continuously added for 8 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 1.2 mL) at 52 h. Isopropyl alcohol (80 mL) was added to the reaction mixture. The resulting precipitate was purified by two reprecipitations from DMF/isopropyl alcohol (6 mL/80 mL). A mixed solvent (THF:water = 9:1, 40 mL) was added to the resulting precipitate, and the insoluble substance was separated by filtration. The obtained solution was then dried by evaporation. The resulting polymer was dissolved in water (40 mL), and the insoluble part was separated by filtration. The final aqueous solution of the polymer, which is soluble in both THF:water = 9:1 and water, was freeze-dried (0.346 g, yield: 27.5%). The other polymers were similarly prepared.

### (c) Branched polymer for light harvesting

Figure S7 shows the schedule for preparing the branched polymer by the continuous addition of the monomer.

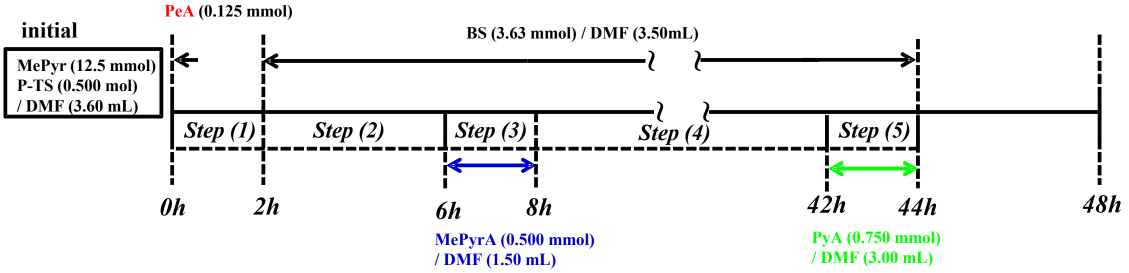


**Figure S7.** Schedule for the continuous addition polymerization of branched polymers.

**Py(6)-Pe(1)** was prepared as follows:

Solution-J: MePyr (12.5 mmol), p-TS (0.50 mmol) in DMF (3.6 mL).

Solution-K: BS (3.63 mmol) in DMF (3.5 mL)

Solution-L: 1-Methyl-2-pyrrolecarboxaldehyde (MePyrA, 0.50 mmol) in DMF (1.5 mL)

Solution-M: PyA (0.75 mmol) in DMF (3.0 mL)

3-Perylenecarboxaldehyde (PeA, 0.125 mmol) was added to Solution-J with stirring (300 rpm) at 10 °C for 2 h. Solution-K was continuously added to the reaction mixture for 42 h. At 6 h, Solution-L was continuously added for 2 h. Then, at 42 h, Solution-M was continuously added for 2 h. The reaction was stopped by the addition of a sodium carbonate aqueous solution (5%, 1.2 mL) at 48 h. Isopropyl alcohol (80 mL) was added to the reaction mixture. The resulting precipitate was purified by reprecipitations from two times of DMF/isopropyl alcohol (8 mL/80 mL) and two times of water/isopropyl alcohol (6 mL/80 mL), and then dissolved in water. The polymer was obtained by freeze-drying (0.944 g, yield: 70.4%). Other polymers were similarly prepared.

## 3 A, B-block amphiphilic polymer on the heterophase boundary with the donor and acceptor in different phases

In order to confirm that the A, B-block amphiphilic polymer existed on the heterophase boundary and the donor and the acceptor existed in different phases, fluorescence quenching was conducted using two quenchers: anthraquinone (AQ) as the toluene-soluble component and methylviologen ($MV^{2+}$) as the water-soluble component. Two amphiphilic polymers were prepared containing Pe units either in the hydrophobic or hydrophilic phases. The preparation of a micellar system is discussed below. Figure S8b shows the fluorescence spectra of iPB(non)-BS(Pe) excited at 420 nm and dissolved in an emulsion solvent at 25 °C with an acceptor: AQ ($1.5 \times 10^{-2}$ M) (red line), $MV^{2+}$ ($10^{-4}$ M) (green line), or without an acceptor (blue line). The fluorescence quenching occurred only in the $MV^{2+}$ system, which suggests that the Pe unit exists in the water phase (Figure S8c). However, the fluorescence quenching occurred only in the AQ system for iPB(Pe)-BS(none) (Figure S9b). The Pe unit exists in the toluene phase (Figure S9c). These results confirm that the A, B-block amphiphilic polymer existed on the heterophase boundary and the donor and acceptor moieties were in different phases.

**Preparation of a micellar system:** An amphiphilic polymer (0.010 g) was dissolved in the emulsion solvent (water:toluene = 99:1, 1.0 g) with an ultrasonic homogenizer at 25 °C for 1 min. Then, the resulting solution (0.10 g) was diluted by another emulsion solvent (water:toluene = 99:1, 10.0 g) using an ultrasonic homogenizer for 1 min at 25 °C. An aqueous solution of Triton X (water:Triton X = 9:1, 2.1 g) was added to the solution using an ultrasonic homogenizer for 1 min. Finally, a transparent and stable solution was obtained. The other micellar systems were similarly prepared.

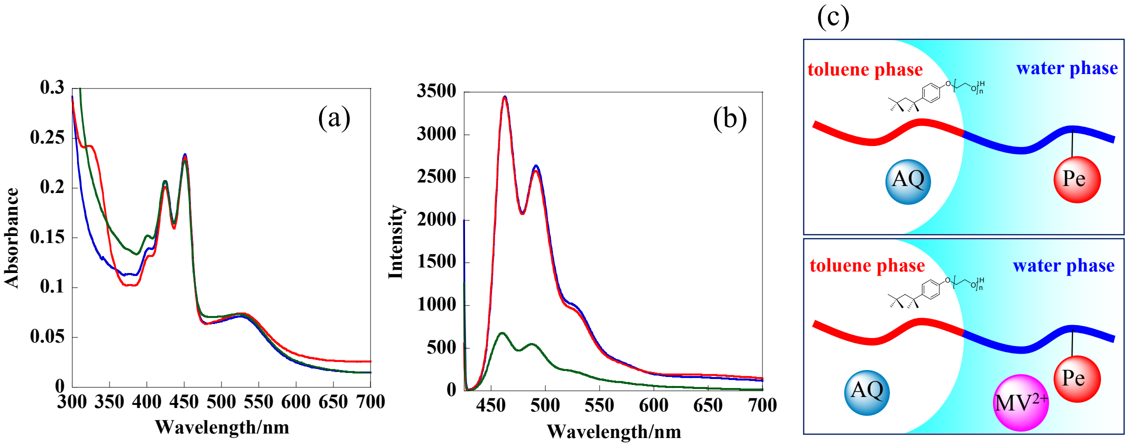


**Figure S8.** (a) Absorption and (b) fluorescence spectra of iPB(none)-BS(Pe) dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C with acceptor: anthraquinone [$1.5 \times 10^{-2}$ M] (red line), methylviologene [$10^{-4}$ M] (green line), or without an acceptor (blue line), [polymer]=0.083 g/L, excited at 420 nm, cell length=1 cm; (c) image of A, B-block amphiphilic polymers in a micellar system.

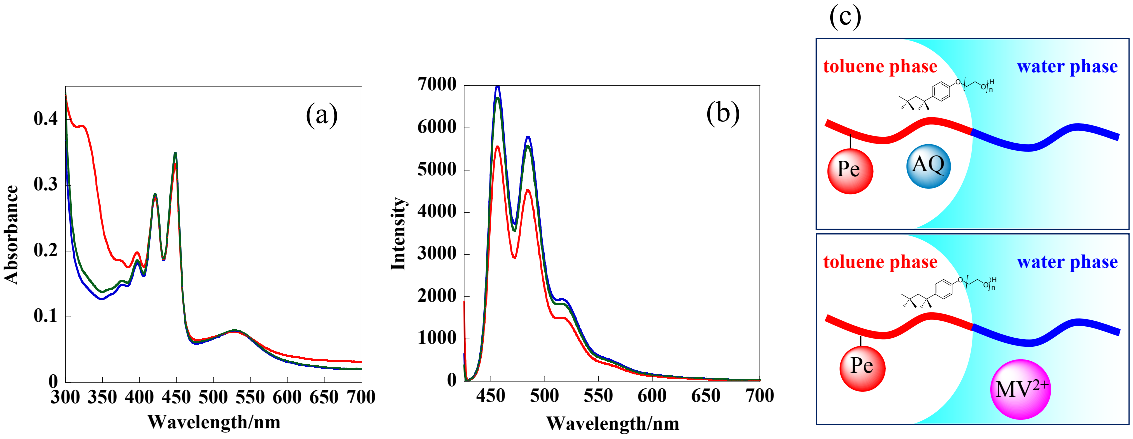


**Figure S9.** (a) Absorption and (b) fluorescence spectra of iPB(Pe)-BS(none) dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C with acceptor: anthraquinone [$1.5 \times 10^{-2}$ M] (red line), methylviologene [$10^{-4}$ M] (green line), or without acceptor (blue line), [polymer]=0.083 g/L, excited at 420 nm, cell length=1 cm; (c) image of A, B-block amphiphilic polymers in a micellar system.

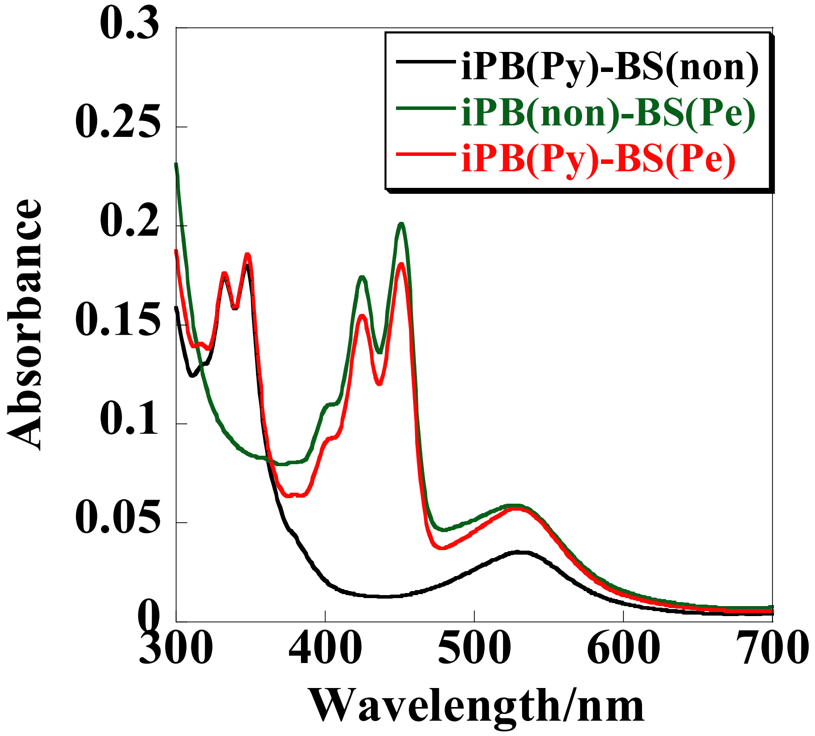


**Figure S10.** Absorption spectra of A, B-block amphiphilic polymers containing Py and Pe units dissolved in a water/toluene emulsion (118/1) including 1.8% Triton X at 25 °C, [polymer]=0.083 g/L, cell length=1 cm.

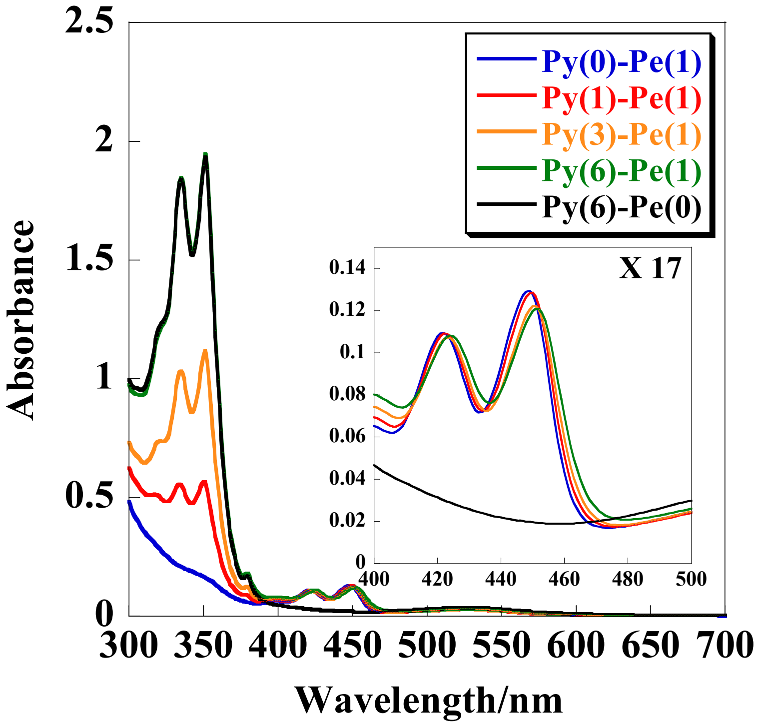


**Figure S11.** Absorption spectra of branched polymers containing high and low amounts of Py and Pe units dissolved in water at 25 °C, abs (420 nm)=0.1, except Py(6)-Pe(0), cell length=1 cm.

## 4 Solvent effects on the fluorescence with respect to Py unit changes

In Figure 3a and Figure 4a, the fluorescence profiles of the Py unit are different from a general emission profile for monomeric Py. This change of the emission profile is due to a solvent effect and/or excimer generation. To clarify the cause of the change, Py-dipyrromethane was prepared, and fluorescence spectra were measured in different mixed solvents of toluene and methanol. The fluorescence profiles changed drastically in different solvents. However, no profile changes were observed at different concentrations. These results indicate that the unusual spectral profile of the Py unit in Figure 3a and Figure 4a reflects the different circumstances, not excimer generation, which are always concentration dependent.

### Py-dipyrromethane (1-methyl-2-((1-methyl-1H-pyrrol-2-yl)(pyren-3-yl)methyl)-1H-pyrrole)

PyA (0.50 mmol) and p-TS (1.70 mmol) were dissolved in MePyr (50.0 mmol, 4.4 mL) at 10 °C. After 20 min, the resulting precipitate was obtained by suction filtration and recrystallized from methanol (5 mg, 3.0%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.05 (m, 8H), 7.54 (d, 1H, J = 8.3Hz), 6.65 (d, 2H, J = 1.6Hz), 6.29 (s, 1H), 6.02 (t, 2H, J = 2.97 Hz), 5.47 (d, 2H, J = 1.2 Hz), 3.42 (s, 6H).

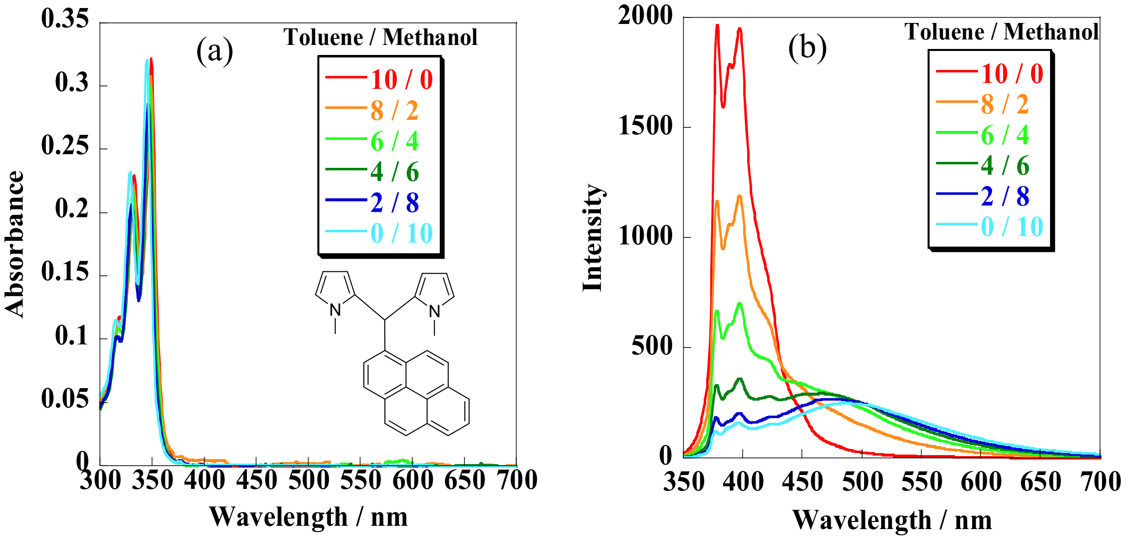


**Figure S12.** (a) Absorption and (b) fluorescence spectra of Py-dipyrromethane dissolved in mixed solvents (toluene/methanol = 10/0, 8/2, 6/4, 4/6, 2/8, 0/10) at 25 °C. The samples were prepared by the absorbance (0.2) at 330 nm, excited at 330 nm, cell length=1 cm.

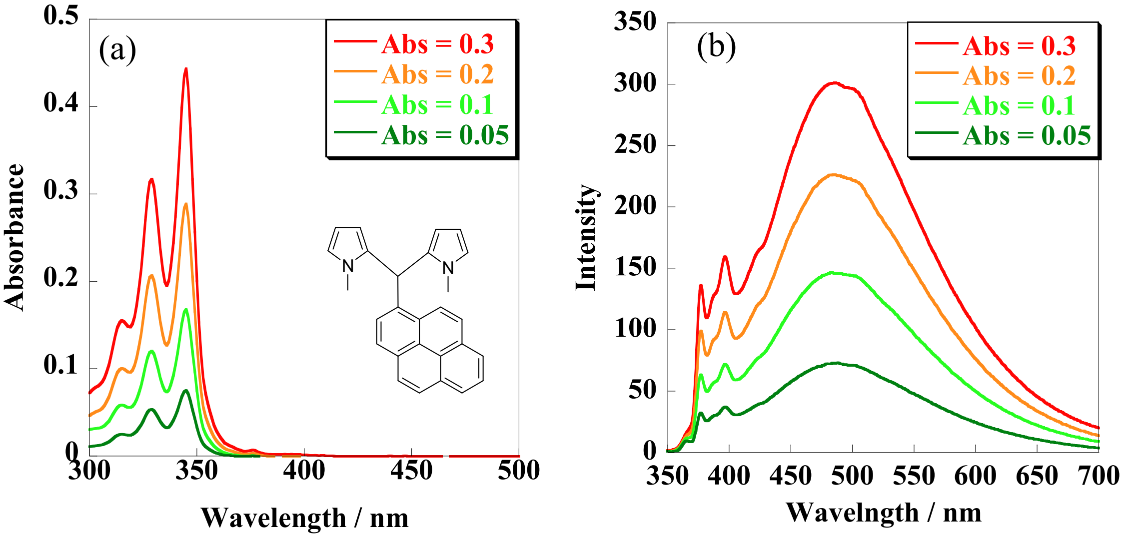


**Figure S13.** (a) Absorption and (b) fluorescence spectra of Py-dipyrromethane dissolved in methanol at 25 °C. The samples were prepared by the absorbance (0.05), (0.1), (0.2), and (0.3) at 330 nm, respectively, excited at 330 nm (b), cell length=1 cm.

## 5 Additional information of polymers and monomers.

### NMR spectra

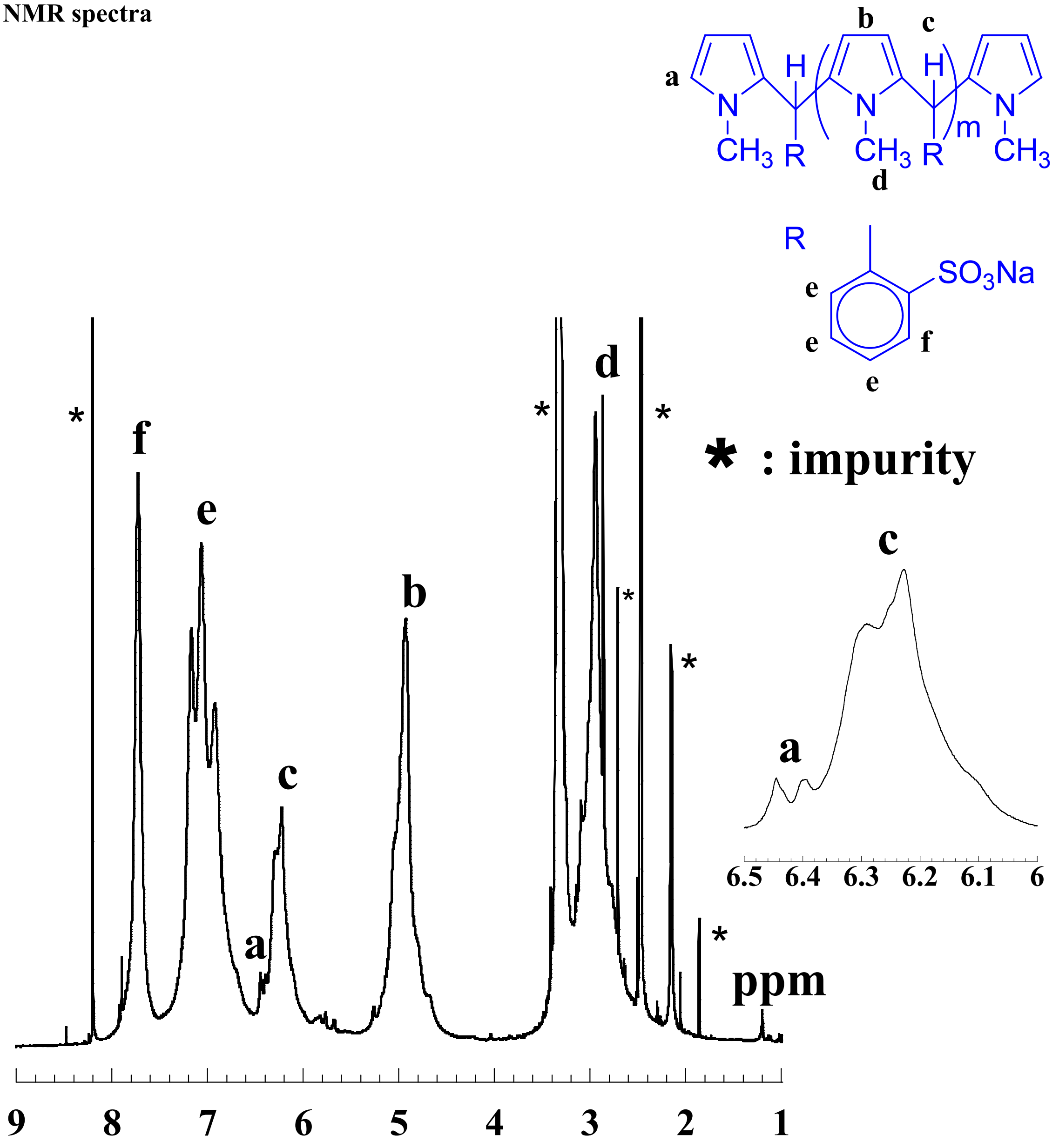


**Figure S14.** $^{1}$H-NMR spectrum of MePyr-BS (8day) polymer in DMSO-d$^{6}$.

**$^{1}$H NMR spectrum of MePyr-BS (8 day) polymer.** Figure S14 shows the chemical structure and the NMR spectrum of MePyr-BS (8 day) polymer. Although the spectrum broadening is observed in the polymer, it also showed the signals of the polymer proton. The peaks (6.47, 4.94 and 2.95 ppm) assigned to MePyr protons (a: terminal, b and d). The peaks (7.08 and 7.73 ppm) assigned to BS protons (e and f).

The number-average molecular weight was estimated by the signal intensity ratio of the terminal α-proton (a) and another proton attached to the benzene ring adjacent to the sulfo group (f).

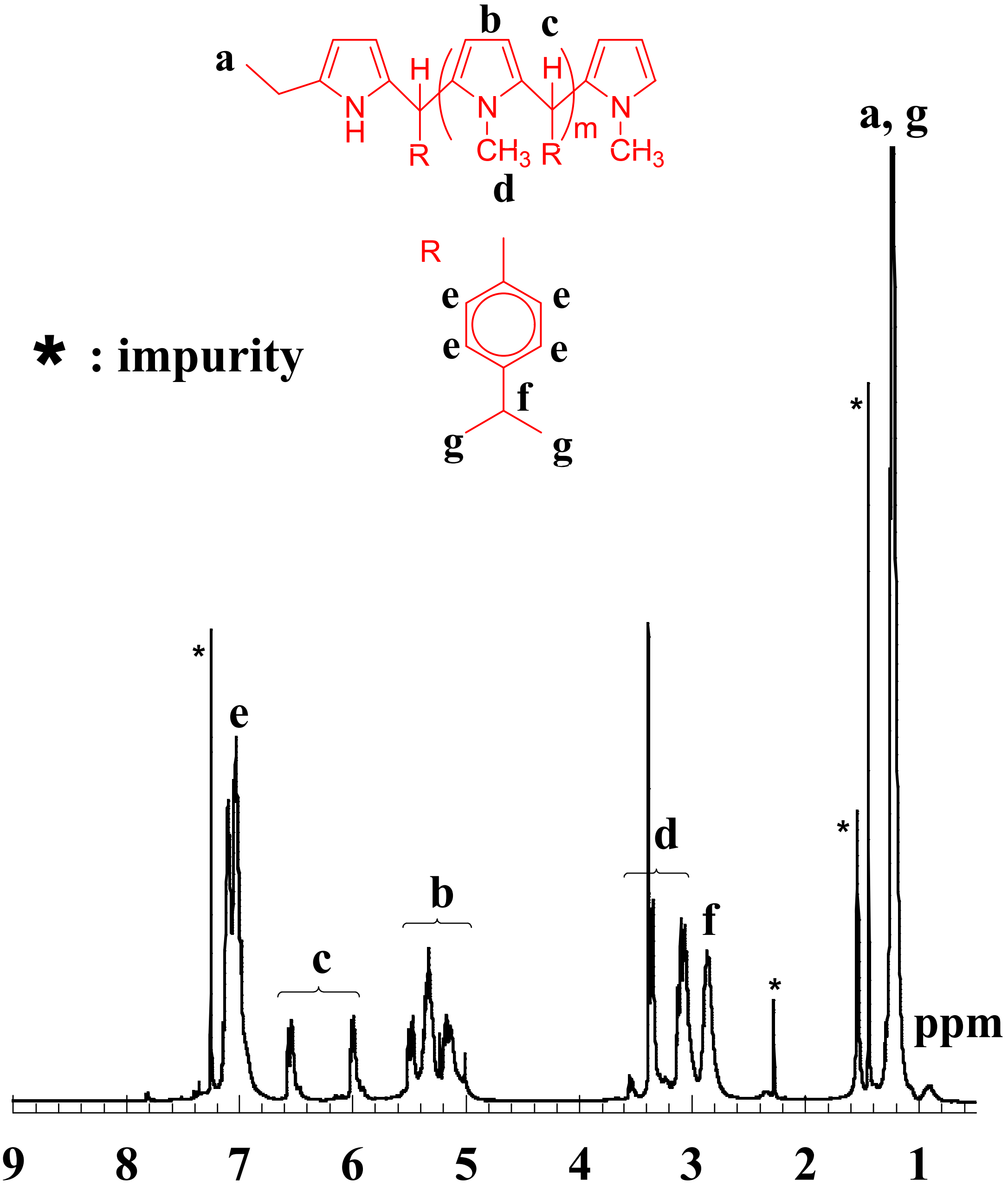
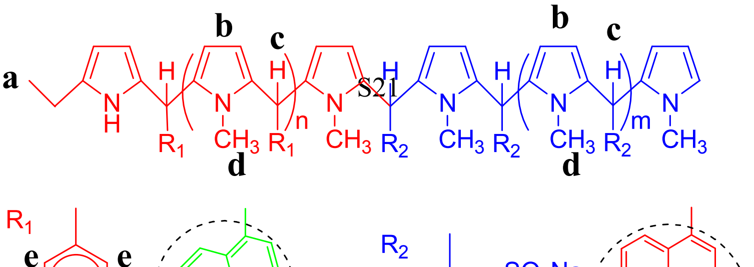


**Figure S15.** $^1$H-NMR spectrum of MePyr-iPB polymer in $CDCl_3$.

**$^1$H NMR spectrum of hydrophobic polymer (MePyr-iPB).** Figure S15 shows the chemical structure and the NMR spectrum of MePyr-iPB polymer. It showed the signals of the polymer proton. The peaks from 3.0 ppm to 3.5 ppm and the peaks from 4.85 to 5.65 ppm assigned to MePyr protons (d and b). The peaks (7.05, 2.85 and 1.21 ppm) assigned to iPB protons (e, f and g).



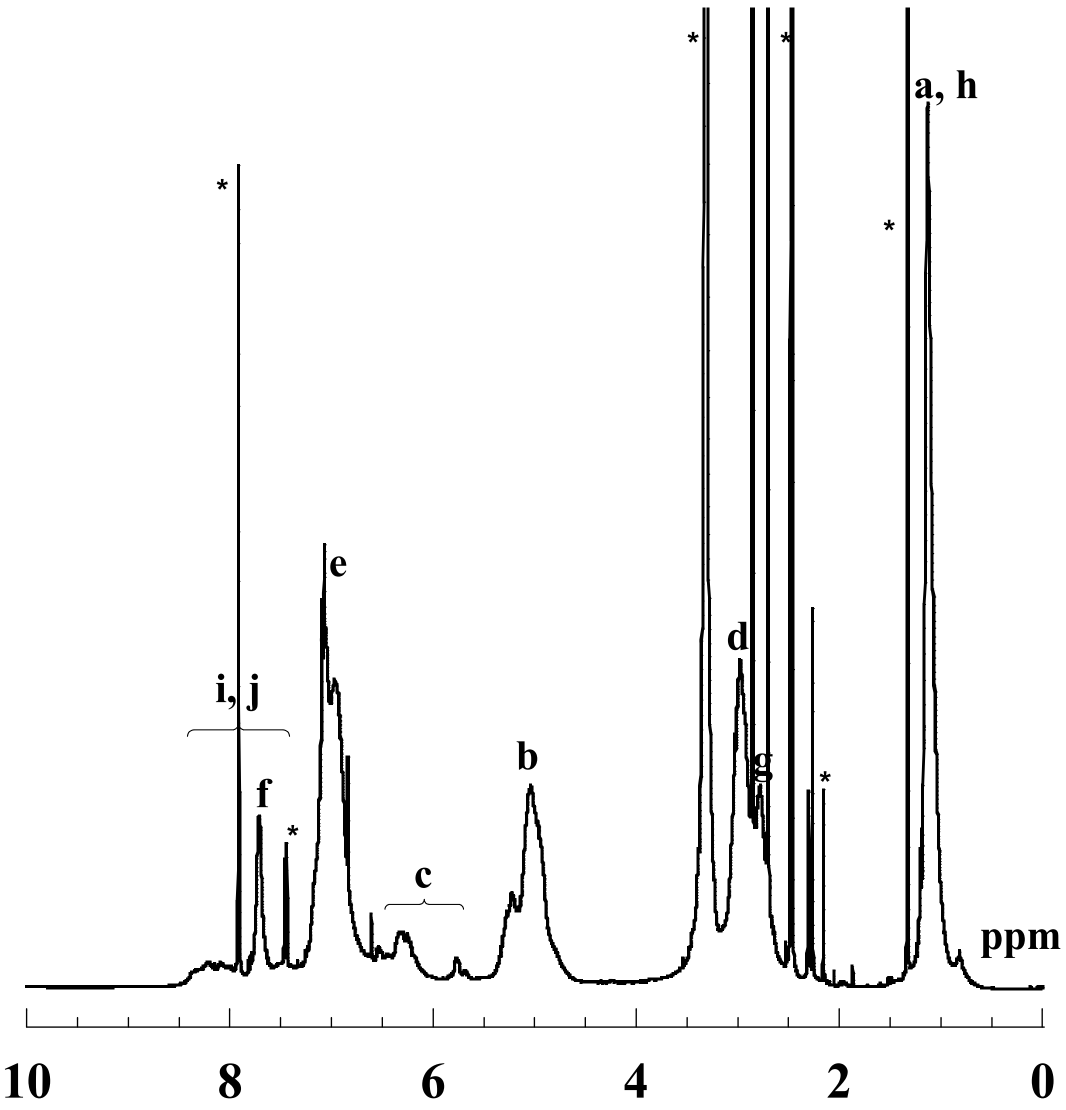


**Figure S16.** $^1$H-NMR spectrum of A, B-block amphiphilic polymer in DMSO-d$^6$.

**$^1$H NMR spectrum of A, B-block amphiphilic polymer (iPB(Py)-BS(Pe)).** Figure S16 shows the chemical structure and the NMR spectrum of A, B-block amphiphilic polymer. Based on Figure S14 and S15, the ratio of the hydrophobic part and hydrophilic part in the A, B-block amphiphilic polymer was 1.2:1, because the intensity ratio of signals of the iPB proton $H_h$ (1.21 ppm) to the BS proton $H_f$ (7.73 ppm) was 7.2:1. The peaks from 7.5 to 8.5 ppm assigned to Py and Pe protons (i and j).

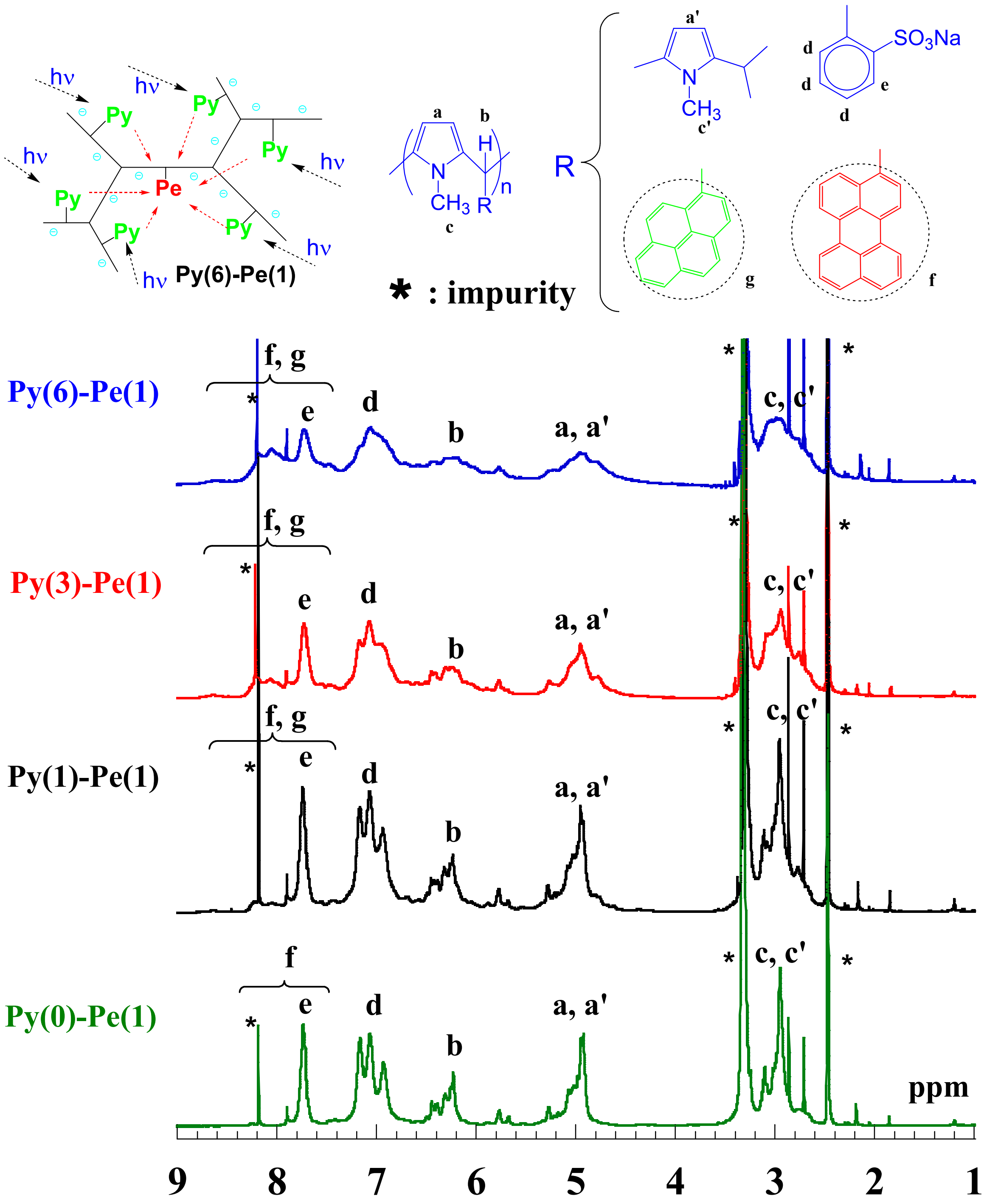


**Figure S17.** $^1$H-NMR spectra of branched polymers in DMSO-d$^6$.

**$^1$H NMR spectra of branched polymers.** Figure S17 shows the chemical structures and the NMR spectra of branched polymers. The peaks from 7.5 to 8.5 ppm assigned to Py and Pe protons (g and f). From Py(0)-Pe(1) to Py(6)-Pe(1), these signals become stronger as the Py content increases.

## The reactivity of other monomers

Pyrrole is usable in this polymerization. Thiophene and furan is not usable in this addition-condensation under the mild condition (e.g. at room temperature) because of lower reactivity.

For benzene derivatives, 1,2,3-trihydroxy benzene is usable in the addition-condensation polymerization. However, reactivity ratio of dimer to monomer is only 8:1 (methylpyrrole system 240:1). Therefore, we have not yet succeeded in the structure controlled polymerization in 1,2,3-trihydroxy benzene system.

Many aldehydes are usable in the polymerization. However, the reactivity of benzaldehyde-2-sulfonic acid sodium salt (BS) is very high, therefore, addition time control is important to introduce other aldehydes.