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Synthesis and properties of thermotropic liquid-crystalline polyesters containing 9,10-diphenylanthracene moiety in the main chain

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Abstract We synthesized thermotropic liquid-crystalline polyesters in which 9,10-diphenylanthracene moieties are incorporated into the main chain type of polyester forming the chiral smectic C (Sm C*). The polymers were prepared by the isopropyltitanate-catalyzed reaction of biphenyldicarboxylic acid and the corresponding diols, with different ratios of diol of 9,10-diphenylanthracene moiety to the alkane diols (1, 5, and 10 mol %) under nitrogen atmosphere. The polymers exhibited thermotropic liquid crystals despite the presence of a bulky diphenylanthracene moiety in the main chain. The circular dichroism spectra revealed that a Sm C* phase was formed in the polymer with 1 mol % of anthracene moiety, although only an Sm A phase was formed in the other polymers. This is the first example of a Sm C* polyester containing a diphenylanthracene moiety in the main chain. Furthermore, we measured the optical properties of the polymers and found that they exhibited very high fluorescent efficiency. The fluorescence spectra of the thin film differed from that of a CH_2Cl_2 solution.

Keywords Liquid crystal · Polyester · 9,10-Diphenylanthracene · Fluorescence · Chiral polymer

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Dedicated to Professor Kazuhiko Mizuno for his outstanding contribution to organic photochemistry.

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Introduction

Recently, much attention has been paid to organic light-emitting diodes (OLEDs) such as organic electroluminescent devices and organic lasers [1–20]. It is essential to develop a highly luminescent dye for use in these diodes. A large number of luminescent dyes have been synthesized. In particular, 9,10-diphenylanthracene exhibits excellent fluorescent properties (e.g., high quantum efficiency, pure blue fluorescence, and thermal stability) [21–27]. A variety of polymers containing 9,10-diphenylanthracene moieties have been synthesized and researched because of their potential applications in optical devices [21–25]. The polymers are soluble in organic solvents for easy processability, and the strength of the polymer films enables flexible devices to be realized. In addition, by introducing a diphenylanthracene moiety into the polymer main chain, intermolecular quenching can be prevented efficiently and high luminous efficiency can be expected in solid-state-like films. Therefore, diphenylanthracene and its related polymers are expected to be profitable for applications in various optical devices such as OLEDs [22–28].

A liquid crystal (LC)-laser system is one such optical device. Cholesteric, chiral smectic C (Sm C*), and some LCs are known to have a helical structure. When a fluorescent dye is injected into these materials, the emission is enhanced because of the helical structure and thus laser oscillation can be observed. Such LC-laser systems are expected to have tunable wavelengths and very small size [29–35]. In addition, in the case of such LC-laser systems, high-luminous-efficiency polymers such as diphenylanthracene are very attractive materials, because they can use energy more efficiently. However, Jin et al. [21] reported that the diphenylanthracene moieties in the polymer main chain inhibit the arrangement of LC molecules, and hence, these polymers cannot form a liquid-crystalline phase.

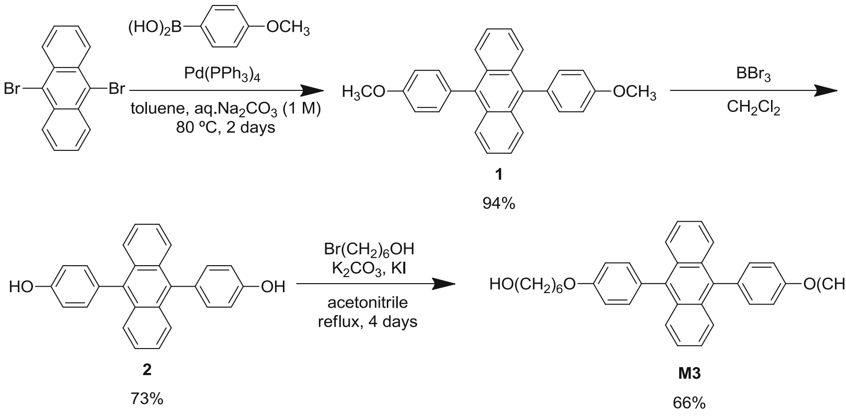
Here, we report the first example of a Sm C* polyester containing a 9,10-diphenylanthracene moiety in the main chain, in which a helical structure is formed along the average polymer chain axis [36–38], and investigate the effect of diphenylanthracene moieties on the liquid-crystalline behavior. The partly introduced diphenylanthracene group is expected to act as a laser dye for LC-lasers.

Results and discussion

Synthesis and characterization

A 9,10-diphenylanthracene monomer, which is a fluorescent moiety of the polymer, was synthesized according to Scheme 1. First, a 4-methoxyphenyl group was introduced to 9,10-dibromoanthracene by Suzuki–Miyaura coupling [39, 40]. Then, after the phenol moiety was deprotected by BBr_3, alkyl chains were introduced as a spacer by Williamson ether synthesis. The overall yield was 45 %.

The polymerization was carried out according to the procedure in our previous report [36]. The polymers were synthesized by melt transesterification of dimethyl 4,4′-biphenyldicarboxylate and an appropriate mixture of 1,6-hexanediol (**M1**), (*S*)-2-methyl-1,4-butanediol (**M2**), and anthracene derivative diol (**M3**) in the



Scheme 1 Synthesis of anthracene monomer

Table 1 Properties of polymers **1–3**

	Molar ratio (**M1** + **M2**[a]:**M3**)	Yield (%)	M_n^b	M_w/M_n^b
Polymer **1**	99:1	63	3,600	1.7
Polymer **2**	95:5	65	2,600	1.5
Polymer **3**	90:10	70	3,200	1.5

[a] **M1**:**M2** = 3:7

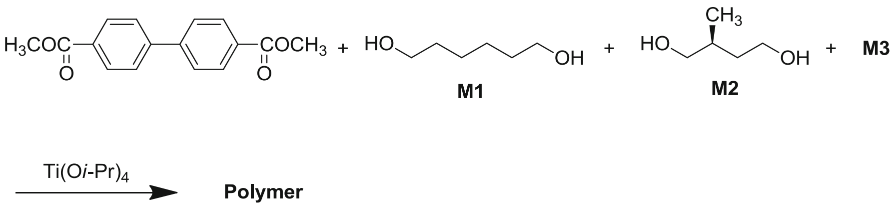
[b] Determined by GPC (eluent: THF, polystyrene standards)

presence of isopropyltitanate (Scheme 2). According to the previous study [38], BB-4*/6(70/30) polyester was selected as a based polyester with **M1** and **M2** in molar ratio of 3:7 since it formed a Sm C* having pitch of 400–450 nm. Three polymers having different ratios of 9,10-diphenylanthracene-based **M3** (1, 5, and 10 %) to the sum of **M1** and **M2** were synthesized (Table 1).

The polymerization results are summarized in Table 1. The structures of the obtained polymers were confirmed by ^{1}H nuclear magnetic resonance (NMR) and Fourier-transform infrared (FT-IR) spectra. Figure 1 shows the ^{1}H NMR spectrum of polymer **3**. ^{1}H NMR integration confirmed that the main chain contained 10 mol % of diphenylanthracene moieties, 27 and 44 mol % of **M1** and **M2**, respectively, and 19 mol % methoxy ester. The number-average molecular weight (M_n) determined by ^{1}H NMR was about 3,400. The amount of diphenylanthracene moieties in polymer **1** was too little for them to be observed in the ^{1}H NMR spectrum. However, by using gel permeation chromatography (GPC) (detecting wavelength changed from 254 to 350 nm), it was confirmed that the diphenylanthracene moiety existed in the main chains of polymers **1–3**.

Liquid crystallinity

The thermal behaviors of polymers **1–3** were investigated using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The curves in Fig. 2a, b show the DSC thermograms of polymers **1** and **3**, respectively. Polymer **1** showed a phase transition similar to that of the based BB-4*/6(70/30) polyester



Scheme 2 Synthesis of liquid-crystalline polymers

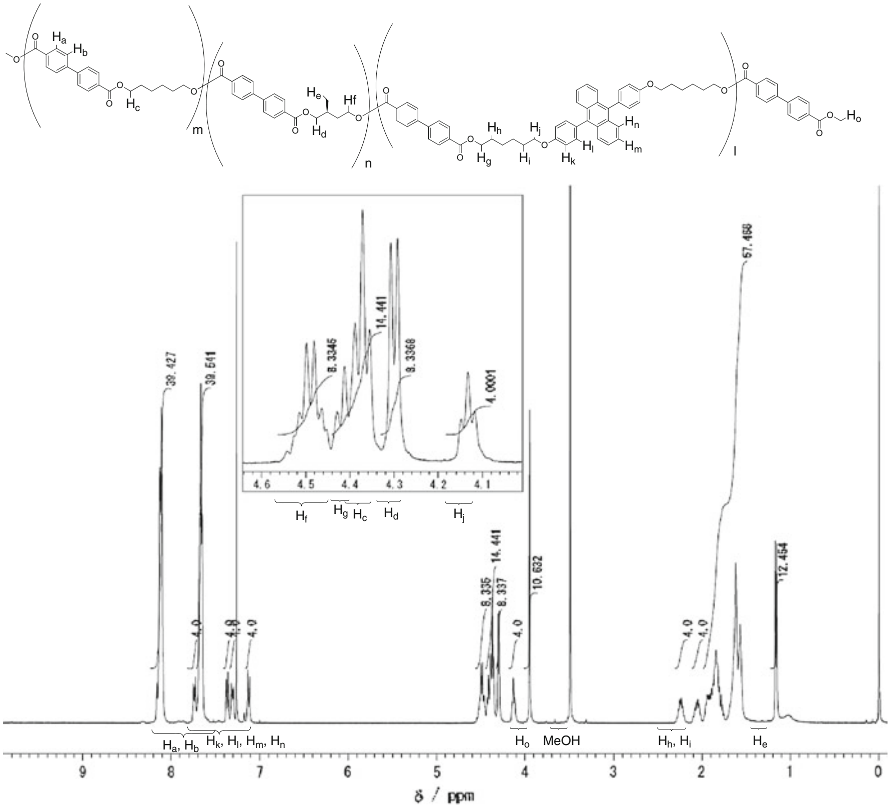


Fig. 1 ^{1}H NMR spectrum of polymer **3** (400 MHz, $CDCl_3$)

[crystal ↔ Sm C* ↔ Sm A ↔ isotropic (Iso)] [38]. Although the Sm C*-Sm A transition is hardly detected from the DSC curve because of its small enthalpy change, it is clearly detected from the POM observation; very fine fan-shaped textures of Sm A are developed at 220 °C on cooling from the isotropic phase, and then at 160 °C, a fan-shaped Sm A texture transforms to a broken-fan-shaped texture characteristic of Sm C* [38]. The POM images of respective textures for polymer **1** at 170 and 80 °C are shown in Fig. 3a and b, respectively. On the other hand, polymer **3** did not show the evident peaks in DSC thermogram (Fig. 2b). However, crystal ↔ Sm A ↔ Iso transitions could be detected from the POM

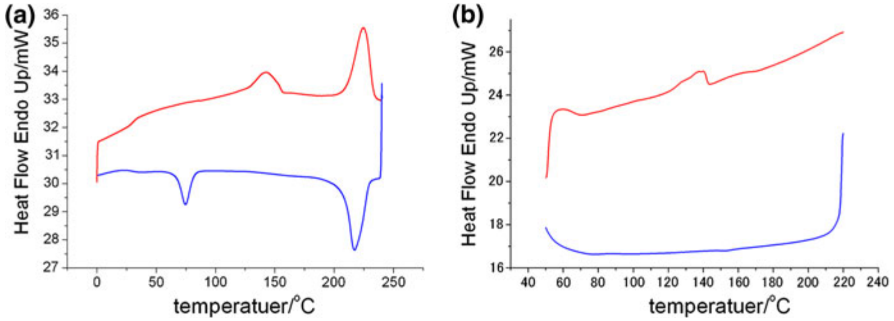


Fig. 2 DSC thermograms of polymer **1** (**a**) and **3** (**b**)

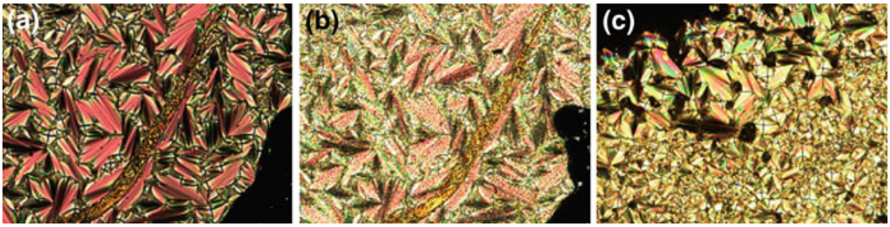


Fig. 3 POM images of polymers **1** and **3**. **a** *Fan-shaped* texture at 170 °C for polymer **1**. **b** *Broken fan-shaped* texture at 80 °C for polymer **1**. **c** *Fan-shaped* texture at 160 °C for polymer **3**

observation for polymer **3**, in which the fan-shaped texture appeared at 160 °C (Fig. 3c). Moreover, polymer **2** showed similar results to polymer **3**.

For polymer **1**, the Sm C* formation from the Sm A was also clarified from the observation of the circular dichroism (CD) reflection spectrum which is due to the formation of helical structure. The CD spectra observed for the homeotropically aligned sample are shown in Fig. 4. The reflection band is clearly observed with the peak maximum around 440 nm, although it disappears on heating to the Sm A phase. The peak maximum position is nearly equal to that of the based BB-4*/6(70/30) polyester. The above two results show that the Sm A–Sm C* transition is around 160 °C.

The phase-transition temperatures of polymer **1**–**3** are summarized in Table 2. The introduction of diphenylanthracene, as a foreign compound from the BB-6 polyester, decreased the phase-transition temperatures and then diminished the Sm C* phase with content above 5 %, although the Sm A phase was still formed for the high content (10 %).

The phase behaviors of polymer **1** and **3** were also detected by wide-angle X-ray diffraction. The temperature dependence of the layer spacing and tilt angles are shown in Fig. 5. In the case of polymer **1**, the layer spacing increased with temperature whereas the tilt angles decreased. These values became constant at around 160 °C. This result indicates that the phase transition (Sm C* ↔ Sm A) occurs at around 160 °C. In contrast, in the case of polymer **3**, the layer spacing and

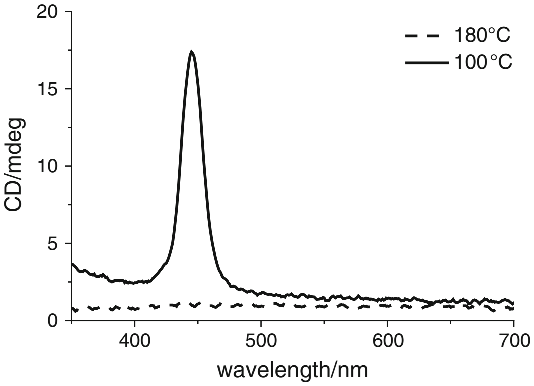


Fig. 4 CD spectra of polymer **1** at 180 °C (*broken line*) and 100 °C (*solid line*). Here, the spectra is observed for the homeotropic aligned sample that is prepared by sharing the Sm A phase between glasses [38]

Table 2 Phase-transition temperatures for polymers **1**–**3**

	Transition temperature[a]/°C
Polymer **1**	Iso 224.8 ↔ Sm A 160 ↔ Sm C* 142.7 ↔ T_g 29.8
Polymer **2**	Iso 220.2 ↔ Sm A 140.6 ↔ Cr
Polymer **3**	Iso 200–220 ↔ Sm A 137.4 ↔ Cr

[a] Polymers **1**–**3** were cooled at a rate of 10 °C min^{-1}

tilt angles did not change at all, indicating the formation of Sm A in the total mesophase temperature region, as detected in POM observation.

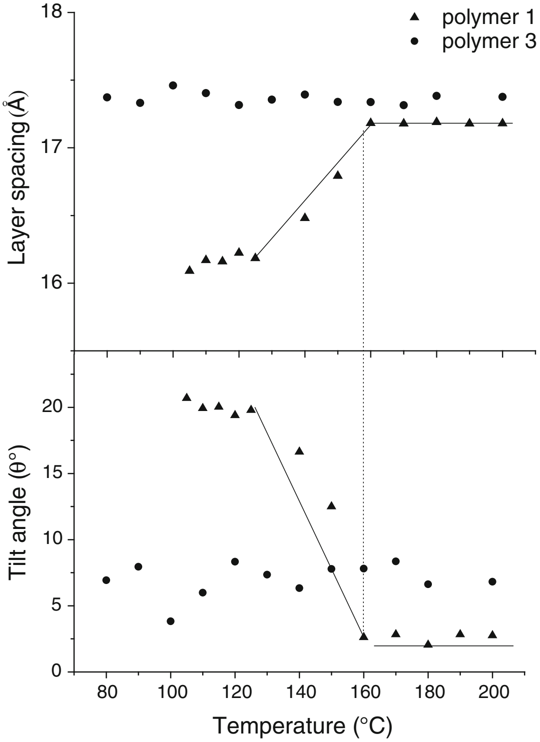
From these results, it is considered that excess amount of anthracene moiety inhibits the formation of Sm C*. It is well known that these helical structures of LCs are very sensitive to aspects of the environment such as the nature of the chiral dopant, temperature, mechanical stress, and field conditions [29–35, 41]. In this case, a small amount of diphenylanthracene moiety may have changed the balance of the environment, interrupting the formation of a helical structure, while even a high content (10 mol %) in the main chain does not prevent formation of a liquid-crystalline phase.

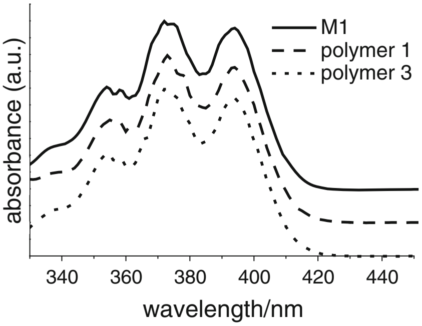
Optical properties

The normalized absorption and fluorescence spectra of **M3**, polymer **1**, and polymer **3** are shown in Fig. 6, and their optical properties are summarized in Table 3. To compare their fluorescence efficiencies, the relative fluorescence quantum yield (Φ_F) emitted from anthracene moiety in polymers **1** and **3** were calculated as the **M3** standard (the calculation method is summarized in the “Experimental” section). There exist no differences between the spectra of monomers and polymers. However, the relative Φ_F of all the polymers are lower than that of **M3**.

We measured the fluorescence spectrum of polymer **1** in a film state (Fig. 7). The fluorescence peak was observed at 437 nm. The value was shifted by 10 nm from that of the polymer solution. Remarkably, the fluorescence spectrum of the film perfectly overlapped the CD spectrum of polymer **1** (Fig. 8). This indicates the possibility of interaction between the fluorescence of our synthesized polymers and

Fig. 5 Temperature dependence of layer spacing and tilt angles (*filled triangles* polymer **1**, *filled circles* polymer **3**)





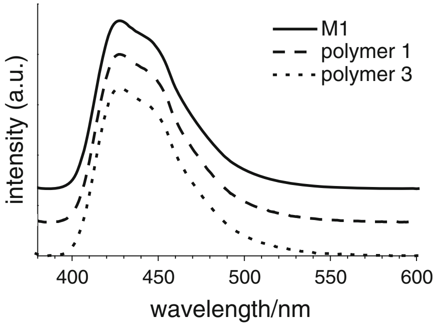


Fig. 6 Normalized absorption and fluorescence spectra of **M3**, polymer **1**, and polymer **3** measured in CH_2Cl_2

their helical structure [42], suggesting the possibility of laser oscillation. The realization of laser oscillation is now in progress.

Conclusions

We synthesized new liquid-crystalline polyesters, polymer **1**–**3**, containing a 9,10-diphenylanthracene moiety in the main chain. These polymers exhibited

Table 3 Optical properties of **M3**, polymer **1**, and polymer **3**

	λ_{abs} (nm)[a]	λ_{em} (nm)[a,b]	Φ_F^a
M3	358, 375, 394	427	0.67[c]
Polymer **1**	358, 373, 394	427	0.50[d]
Polymer **3**	358, 373, 393	427	0.51[d]

[a] Measured in de-aerated CH_2Cl_2

[b] Excited at absorption maxima

[c] Absolute quantum yield

[d] Calculated by using **M3** as a standard

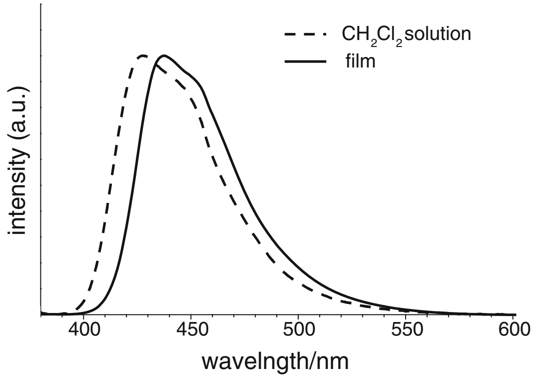


Fig. 7 Fluorescence spectra of polymer **1** in CH_2Cl_2 and film state (film thickness: 25 μm)

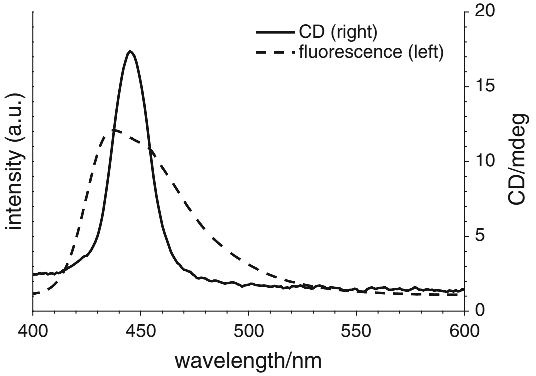


Fig. 8 Fluorescence and CD spectra of polymer **1**

liquid-crystalline behavior despite the presence of a bulky fluorescence moiety in the main chain. A Sm C* phase was observed in polymer **1** with 1 mol % of anthracene moiety similarly to in the based BB–4*/6(70/30) polyester. This is the first example of a Sm C* polyester containing a bulky fluorescent moiety in the main chain. On the other hand, a Sm C* phase disappears in the polymers containing 5 and 10 mol % of anthracene moiety, although the ability for formation of Sm A is sustained. This indicates that an excessive amount of dye molecules inhibits only the formation of the Sm C* phase. These polymers exhibit high quantum yields (ca. $\Phi_F = 0.51$). In the case of polymer **1**, overlap of the fluorescence and CD spectra was observed, indicating the possibility of laser oscillation in the helical field of Sm C*.

Experimental

Instruments

Infrared (IR) spectra were recorded on a JASCO FT-IR 460 plus spectrometer. Nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ on a JEOL LNM-EX 400 at room temperature using tetramethylsilane as internal standard. GPC was carried out by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSKgel G3000H_{XL} column) using tetrahydrofuran (THF) as eluent after calibration with polystyrene standards. The thermal behavior was investigated by POM (Leica DM2500P microscopy with a Mettler FP90 hot stage) and differential scanning calorimetry (Perkin Elmer DSC7) with heating and cooling scans performed at 10 °C min^{-1}. X-ray diffraction photographs were taken at different temperatures by using Ni-filtered Cu K_α radiation. The temperature was measured and regulated by using a Mettler FP90 heater. The sample-to-specimen distance was determined by calibration with silicon powder. The reflection spectra of light were measured with Jasco model J-20 and Hitachi model 330 spectrometers. UV–Vis spectra were recorded by a Beckman Coulter DU800 UV–Vis spectrophotometer. Fluorescence spectra were recorded by a JASCO FP-6500 spectrofluorometer. The relative quantum yield was calculated according to Eq. (1), where $\Phi_{F(ref)} = 1.00$ (relative quantum yield in CH_2Cl_2 solution of **M3**), $\Phi_{F(A)}$ are relative Φ_F in CH_2Cl_2 solution of synthesized polymer, PL_A and PL_{ref} are the integrated fluorescence intensityes of the sample and the standard, respectively, UV_A and UV_{ref} are the absorbances of the sample and the standard at the excitation wavelength, respectively, and η_A and η_{ref} are the refractive indices of the corresponding solutions.

$$\phi_{F(A)} = \phi_{F(ref)} \times \frac{PL_A}{UV_A} \times \frac{UV_{ref}}{PL_{ref}} \times \left(\frac{\eta_A}{\eta_{ref}}\right)^2. \tag{1}$$

Materials

Unless otherwise noted, all chemicals were commercially available and used as received. Dibromoanthracene, 3,5-dimethoxyphenylbronic acid, 6-bromohexanol, dimethyl 4,4′-biphenyldicarboxylate, 1,6-hexanediol, (*S*)-2-methyl-1,4-butanediol, and $Pd(PPh_3)_4$ were purchased from TCI, Japan.

9,10-Bis(4-methoxyphenyl)anthracene (**1**)

A solution of 1 M Na_2CO_3 aq (10 mL), toluene (40 mL), 3,5-dimethoxyphenylbronic acid (12 mmol, 1.82 g), dibromoanthracene (3 mmol, 1.00 g), and $Pd(PPh_3)_4$

(0.15 mmol, 0.17 g) was stirred and heated at 80 °C under argon atmosphere for 2 days. The progress of the reaction was checked by thin-layer chromatography. The reaction mixture was extracted with toluene, and the organic layer was dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was washed with THF and recrystallized with chloroform. The objective material, **1**, was obtained as solids (1.1 g, 2.82 mmol, 94 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72–7.75 (m, Ar–H, 4H), 7.39 (d, $J = 8.1$ Hz, Ar–H, 4H), 7.26–7.34 (m, Ar–H, 4H), 7.14 (d, $J = 8.3$, Ar–H, 4H), 3.97 (s, $–OCH_3$, 6H) ppm.

9,10-Bis(4-hydroxyphenyl)anthracene (**2**)

Anhydrated CH_2Cl_2 (30 mL) was added to **1** (2.5 mmol, 0.98 g) under argon atmosphere. Then, BBr_3 in hexane (12.5 mmol, 12.5 mL) was added to the resulting solution at 0 °C. After stirring overnight at room temperature, the mixture was quenched with water. The reaction mixture was extracted with AcOEt, and the organic layer was dried over $MgSO_4$. After removal of solvent under reduced pressure, the solid was recrystallized from acetonitrile. The objective material, **2**, was obtained as solids (0.66 g, 1.83 mmol, 73 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72–7.74 (m, Ar–H, 4H), 7.32–7.35 (m, Ar–H, 8H), 7.07 (d, $J = 7.8$, Hz Ar–H, 4H), 4.88 (s, Ar–OH, 2H) ppm.; FT-IR (KBr): v 3,421, 3,063, 1,605, 1,512, 1,393, 1,246, 1,167, 822, 772 cm^{-1}.

9,10-Bis(4-(4-hydroxyhexyl)oxyphenyl)anthracene (**M3**)

2 (1.40 mmol, 0.51 g), K_2CO_3 (5.00 mmol, 0.69 g), 6-bromohexanol (6.00 mmol, 0.82 mL), and small amount of KI were mixed in acetonitrile (30 mL). The resulting mixture was refluxed for 4 days. Then, the mixture was extracted with $CHCl_3$, washed with water, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the solid was recrystallized from MeOH. The objective material, **M3**, was obtained as solids (0.52 g, 0.92 mmol, 66 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, $J = 3.4$, 6.8 Hz, Ar–H, 4H), 7.37 (d, $J = 8.3$ Hz, Ar–H, 4H), 7.32 (dd, $J = 3.4$, 6.8 Hz, Ar–H, 4H), 7.12 (d, $J = 8.3$ Hz, Ar–H, 4H), 4.12 (t, $J = 6.4$ Hz, $Ar–OCH_2$, 4H), 3.71 (brdt, $J = 4.9$, 6.4 Hz, $-OCH_2$, 4H), 1.92 (tt, $J = 6.4$, 7.3 Hz, 4H), 1.71–1.49 (m, 12H), 1.30 (brt, $J = 4.9$ Hz, -OH, 2H) ppm.; FT-IR (KBr): v 3,422, 2,933, 2,859, 1,605, 1,510, 1,389, 1,241, 1,175, 769 cm^{-1}.

General procedure for polymerization

Dimethyl 4,4′-biphenyldicarboxylate and an appropriate mixture of **M1**, **M2**, **M3**, and small amount of isopropyltitanate were placed in polymerization tube with bubbled nitrogen, and stirred at 230 °C. After polymerization, obtained polymer was dissolved into the minimum volume of chloroform, and reprecipitated in methanol twice. After filtering, the objective polymer was obtained.

Polymer 1

According to the general procedure, 4,4′-biphenyldicarboxylate (270 mg, 1 mmol), **M1** (35 mg, 0.30 mmol), **M2** (72 mg, 0.69 mmol), **M3** (5.6 mg, 0.01 mmol). Yield: 63 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12, 7.65, 4.43–4.54, 4.37, 4.30, 3.94, 2.24, 2.05, 1.75–1.84, 1.16 ppm.; FT-IR (KBr): ν 3,421, 2,955, 2,888, 1,715, 1,607, 1,510, 1,396, 1,274, 1,175, 756 cm^{-1}.

Polymer 2

According to the general procedure, 4,4′-biphenyldicarboxylate (500 mg, 1.85 mmol), **M1** (60 mg, 0.50 mmol), **M2** (120 mg, 1.17 mmol), **M3** (104 mg, 0.185 mmol). Yield: 70 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12, 7.73–7.75, 7.65–7.68, 7.37, 7.30–7.32, 7.12, 4.45–4.54, 4.36–4.43, 4.29–4.31, 4.12–4.15, 3.95, 2.22–2.25, 2.03–2.07, 1.77–1.96, 1.16 ppm.; FT-IR (KBr): ν 3,421, 2,947, 2,864, 1,715, 1,607, 1,512, 1,395, 1,274, 1,175, 1,105, 756 cm^{-1}.

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