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Synthesis of Anthracene-Stacked Oligomers and Polymer

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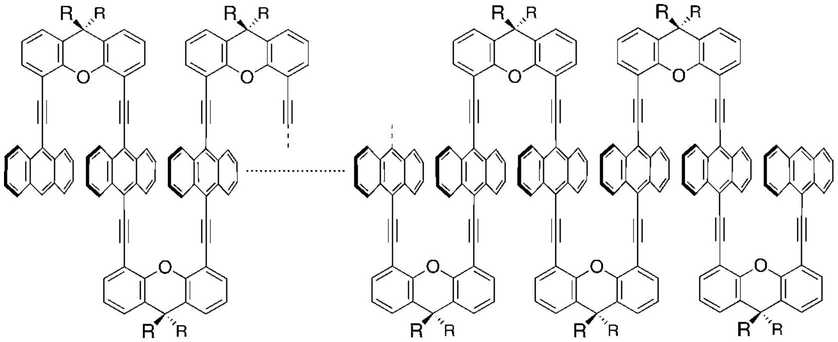
ABSTRACT



Anthracene-stacked oligomers and a polymer were synthesized using a xanthene skeleton as the scaffold, and their structures and properties were fully characterized. Intramolecular $\pi-\pi$ stacking of the anthracene rings in the ground state and excited state was observed.

Currently, construction of oriented and π-stacked structures is one of the topics in the field of synthetic polymer chemistry. Cofacially oriented π-electron systems are of importance in the fields of materials chemistry and biochemistry. This importance can be explained with the help of a few examples. The performance of organic optoelectronic devices strongly depends on the arrangement of the constituent π-electron systems. DNA has face-to-face base pairs stacked in double-stranded main chains. Recently, novel π-stacked polymers such as poly(dibenzofulvene)s,[1] 7,7-diarylnorbornane-containing polymers,[2] side-chain conjugated polymers,[3] cyclophane-containing through-space conjugated polymers,[4−7] and face-to-face ferrocene polymers[8] have been synthesized, and their optical and electrochemical properties have been studied. In addition, xanthene-[9,10] and anthracene-based polymers[11] consisting of layered π-electron systems and polymeric ladderphanes[12] consisting of oriented π-electron systems have also been prepared. These polymers have potential applications in optoelectronic devices and

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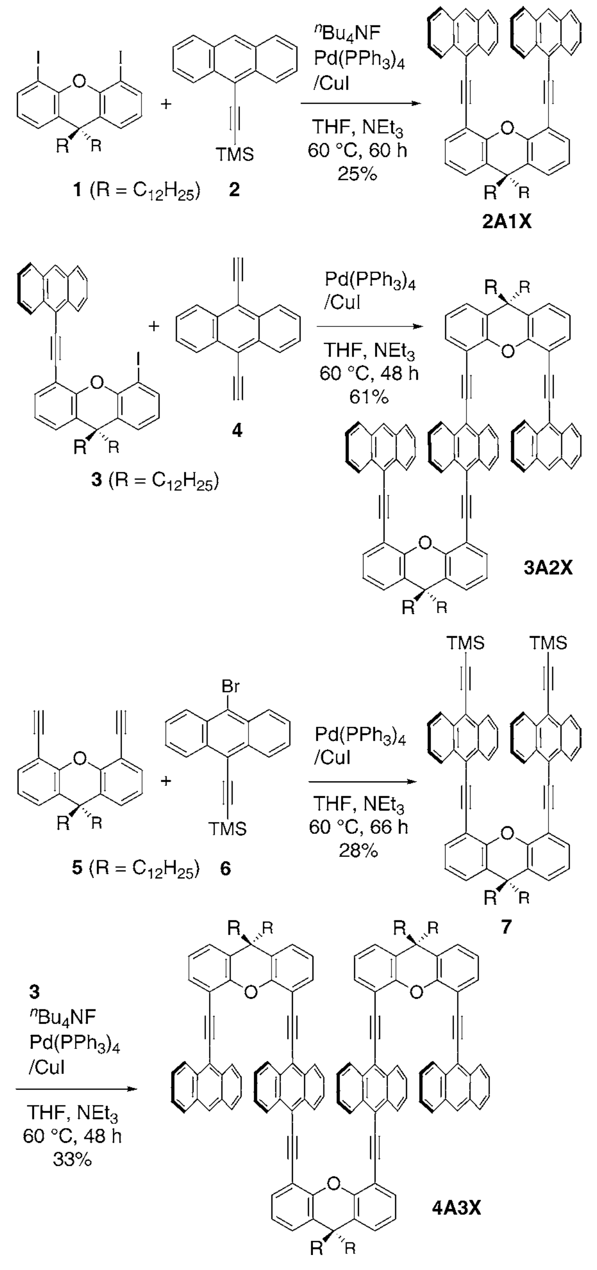
single-molecular devices such as single molecular wires. In addition to these polymers, well-defined aromatic-system-layered oligomers such as anthracene-based trimeric and pentameric porphyrin arrays have been synthesized.[13] We recently synthesized aromatic-ring-layered polymers by using xanthene compounds as scaffolds.[9,10,14] Among them, [2.2]paracyclophane-layered polymers[9] exhibited a photo-excited energy transfer from the layered [2.2]paracyclophanes to the end-capping groups. However, effective $\pi-\pi$ stacking among the layered [2.2]paracyclophanes was not observed in the ground state. This is because of the relatively long distance between the 4- and 5-positions of the xanthene skeleton. Thus, our next target was to construct layered and π-stacked aromatic units in proximity in the polymer backbone. In this study, we selected anthracene as the layered aromatic unit and xanthene as the scaffold. Anthracenes are expected to be facing each other in the polymer chain due to their restricted rotary motion on xanthene and to exhibit $\pi-\pi$ interactions both in the ground state and in the excited state. Herein, we report the synthesis, characterization, and optical properties of a system of anthracene-stacked oligomers and a polymer.

We synthesized anthracene-stacked oligomers **2A1X**, **3A2X**, and **4A3X** containing two, three, and four face-to-face anthracenes, respectively. These oligomers were synthesized by the Sonogashira−Hagihara coupling reaction,[15] as outlined in Scheme 1. The two-anthracene-stacked compound **2A1X** was obtained in 25% isolated yield by the reaction of 9,9-didodecyl-4,5-diiodoxanthene (**1**)[10a,c] with 9-(trimethylsilylethynyl)anthracene (**2**) in the presence of ^{n}Bu$_4$NF. The treatment of a 9-ethynylanthracene-substituted compound (**3**) with 9,10-diethynylanthracene (**4**) gave the three-anthracene-stacked oligomer **3A2X** in 61% yield. The reaction of 9,9-didodecyl-4,5-diethynylxanthene (**5**) with 9-bromo-10-(trimethylsilylethynyl)anthracene (**6**) gave another two-anthracene-stacked compound (**7**) in 28% yield; then, the successive reaction of **7** with **3** in the presence of ^{n}Bu$_4$NF afforded the corresponding four-anthracene-stacked oligomer **4A3X** in 33% yield.

Scheme 1. Synthesis of Anthracene-Stacked Oligomers



The synthesis of anthracene-stacked polymer **P1** is shown in Scheme 2. Monomers **1**, **8**, and **2** were polymerized by the Pd(PPh$_3$)$_4$/CuI catalytic system in the presence of ^{n}Bu$_4$NF to yield the corresponding **P1** in 59% yield after repeated reprecipitation from CHCl$_3$/MeOH. The two dodecyl groups at the 9-position of xanthene contribute to the solubility of the oligomers and polymer in common organic solvents such as CHCl$_3$, CH$_2$Cl$_2$, toluene, and THF. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of **P1** were calculated to be 4600 and 6200, respectively, by gel permeation chromatography (GPC) with polystyrene standards (eluent CHCl$_3$).

The structures of oligomers, polymer, and related compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy

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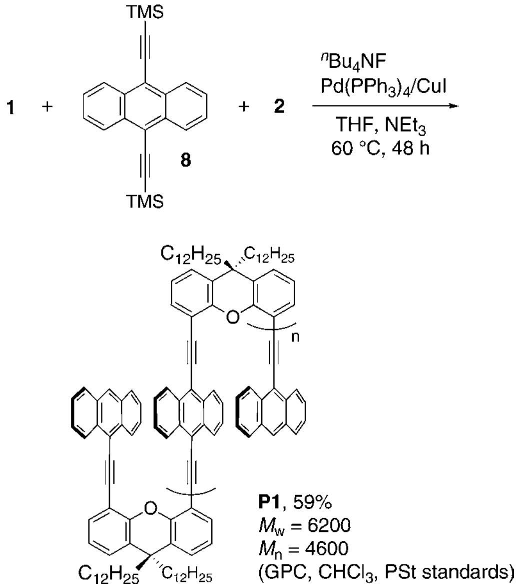
Scheme 2. Synthesis of Anthracene-Stacked Polymer



(Figures S1−S21 in Supporting Information). ^{1}H NMR spectra of **2A1X**, **3A2X**, **4A3X**, and **P1** are summarized in Figure S21. The chemical shifts of anthracene protons were in higher magnetic field than those of common anthracene compounds.[16] Such a chemical shift to a shielding region is attributed to the ring current shielding effect among neighboring anthracene rings. Such an effect is observed in the ^{1}H NMR spectra of a series of 1,8-anthrylene-ethynylene cyclic tetramers[17] as well as [2.2]anthracenophanes.[18] In the ^{1}H NMR spectrum of **2A1X**, signals of the anthracene units appeared at 6.9 ppm, whereas those of the inner anthracene ring in **3A2X** appeared at around 6.5 ppm, as shown in Figure S21. An additional shift was observed in the ^{1}H NMR spectra of **4A3X** and **P1**, and the signals appeared at around 6.3 ppm and 6 ppm (Figure S21), respectively. Thus, with an increasing number of stacked anthracenes, the signals of anthracene protons gradually shifted to the higher magnetic field due to the buttressing effect of the anthracene rings.

In order to gain further insight into their π-stacked structure, we designed and synthesized compound **10**, which has two ferrocenes and an inner anthracene, using two 9,9-dimethylxanthene units as the scaffold, as shown in Figure 1. Ferrocenes and 9,9-dimethylxanthenes were employed for the purpose of enhancing the crystallinity of the compound. Figure 1 also depicts the X-ray structure of **10**. The top view of the ORTEP drawing clearly shows that the cyclopentadienyl rings of the two ferrocenes and the anthracene ring are twisted and have a face-to-face structure. The dihedral angles of the stacked aromatic rings and xanthene scaffolds are 27.2°. The distance between the 4- and 5-positions of xanthene is 4.643 Å, whereas the shortest distance between the intramolecular face-to-face aromatic rings is 3.265 Å. This distance is smaller than the sum of the van der Waals radius of an sp^2 carbon (3.40 Å), suggesting the presence of π−π interactions among the two ferrocenes and the anthracene. Thus, the restricted rotaion of anthracenes in the polymer can be expected, leading to their π-stacked structure.

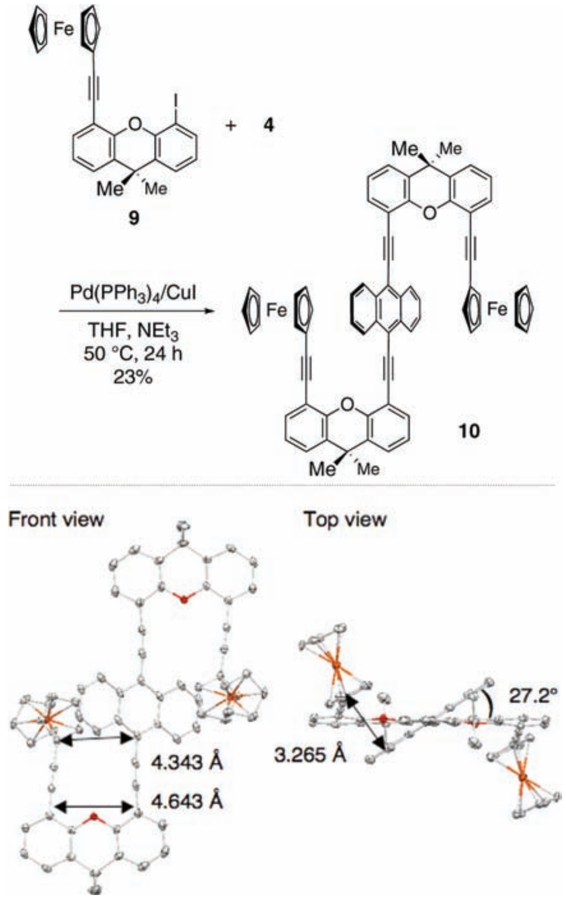


Figure 1. Synthesis and X-ray structure of model compound **10**. Hydrogen atoms are omitted for clarity.

UV−vis absorption spectra and fluorescence spectra of **2A1X**, **3A2X**, **4A3X**, **P1**, and compound **11** in diluted CHCl$_3$ solutions are shown in Figure 2. The molar extinction coefficient of a strong absorption peak at around 250 nm and a broad absorption band at around 400 nm for **2A1X**, **3A2X**, and **4A3X** increased with the number of anthracene rings. The absorption spectra of **2A1X**, **3A2X**, **4A3X**, and **P1** were blue-shifted in comparison with that of **11**, which is derived from the less coplanarity between anthracene and xanthene in the oligomers and polymer. According to the studies on the conformation of 9,10-bis(phenylethynyl)anthracene,[19] the absorption spectrum of **11** exhibits free rotation of anthracene, whereas those of olgomers and polymer show the contribution of the anthracene-twisted structures. Upon normalization of the molar extinction

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(16) In the ^{1}H NMR spectrum of compound **11** (vide supra), signals of the anthracene protons are observed at δ 7.06 and 8.82 ppm (Figure S19 in Supporting Information).

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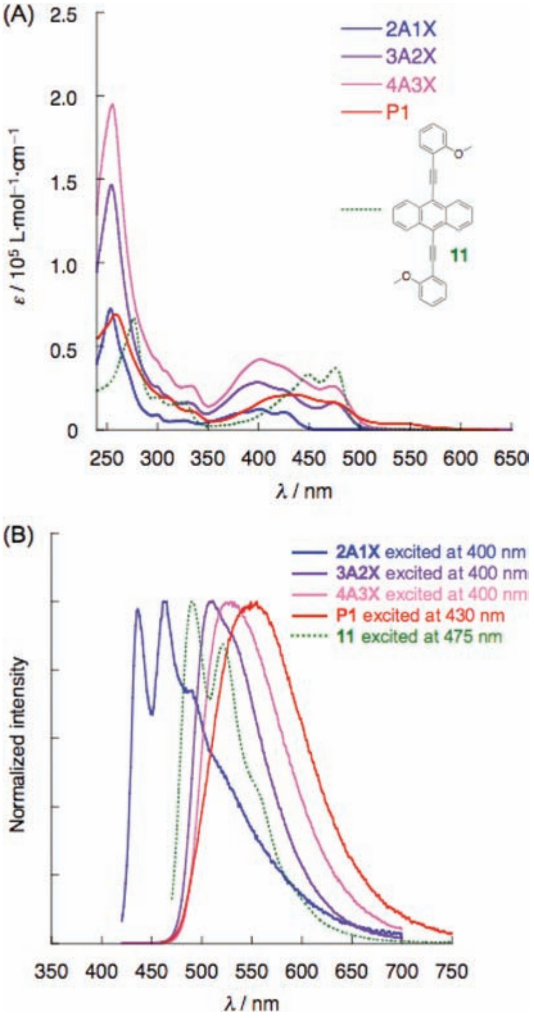

Figure 2. (A) UV−vis absorption and (B) fluorescence spectra of **2A1X**, **3A2X**, **4A3X**, **P1**, and **11** in $CHCl_3$ (1.0×10^{-5} M).

coefficients of the oligomers and polymer with the number of anthracene rings, the coefficients were found to be smaller than that of **11** due to the intramolecular π-stacked structure of the anthracene units in the ground state.

Fluorescence spectra in $CHCl_3$ (1.0×10^{-5} M)[20] revealed that **2A1X** exhibited an emission peak at around 450 nm with a clear vibrational structure similar to that of **11**. Excimer emission was not observed from **2A1X** despite the face-to-face orientation of the two anthracenes. In contrast, the emission peaks of **3A2X**, **4A3X**, and **P1** were broad and featureless, and they appeared in the longer-wavelength region. Fluorescence lifetime measurement of **P1** was performed (Figure S27 in Supporting Information), and it was found that the emission comprised two components. A biexponential fit of the decay afforded short and long decay components with lifetimes (τ) of 4.9 and 34.8 ns, respectively. In consideration of a previously reported observation that the fluorescence lifetime of anthracene in solution is approximately 5 ns,[21] the longer lifetime ($\tau = 34.8$ ns) of **P1** suggests excimer formation in the polymer chain. Thus, **P1** as well as **3A2X** and **4A3X** emit mainly from the excimer state because of the buttressing effect of the anthracene rings. These phenomena are attributed to the intramolecular π-stacked structure of the anthracene units in the excited state.

As a preliminary experiment, the present system was applied to a single molecular wire. As shown in the Scheme S1 in Supporting Information, anthracene-stacked polymer **P2** end-capped with ferrocenes as a fluorescence quencher was synthesized. In diluted $CHCl_3$ solution (1.0×10^{-6} M),[20] photoexcited energy or electron was intramolecularly transferred to both terminals, and the photoluminescence of anthracenes was effectively quenched (Figure S28 in Supporting Information).

In conclusion, anthracene-stacked oligomers and a polymer were synthesized using a xanthene skeleton as the scaffold, and their structures and properties were fully characterized. NMR, UV−vis absorption spectroscopy, and X-ray crystallography revealed that $\pi-\pi$ interactions were present in the anthracene layer in the ground state. The π-stacked structure induced intramolecular excimer formation of the anthracene rings. Thus, we succeeded in the construction of a π-stacked structure using a xanthene scaffold. This class of polymers consisting of stacked aromatic rings has potential application to the single molecular wires, which was demonstrated experimentally in the polymer with quencher units at the polymer chain ends. We are currently extending our research to the design and synthesis of π-stacked oligomers and polymers, which transfer energy or electrons in one direction.

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Supporting Information Available: Experimental details and an X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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