Angewandte
Chemie

Oligo(2,6-anthrylene)s: Acene–Oligomer Approach for Organic Field-Effect Transistors**

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Anthracene has been widely studied as an organic photoconductor during the past five decades.[1] Hole mobilities in anthracene single crystals were measured by the time-of-flight photocurrent technique and were found to reach up to 3 $cm^2V^{-1}s^{-1}$ at 300 K.[2] Although anthracene may be a good candidate for a p-type semiconductor for organic field-effect transistors (OFETs),[3] FET activity has not yet been observed. Recently, OFETs with tetracene were realized and showed a hole mobility of 0.01 $cm^2V^{-1}s^{-1}$ on SiO_2/Si.[4] Of all the OFET materials reported so far, the highest field-effect mobility has been recorded in pentacene (0.3–0.7 $cm^2V^{-1}s^{-1}$ on SiO_2/Si and 1.5 $cm^2V^{-1}s^{-1}$ on chemically modified SiO_2/Si).[5] The HOMO energy level in linear [n]acenes ($n = 2$: naphthalene, 3: anthracene, 4: tetracene, 5: pentacene) significantly increases with increasing n, which facilitates the formation of radical cations (holes) at the interface between a dielectric and a semiconducting layer. Furthermore, the extended π system of a higher acene enhances the intermolecular overlap of π–π systems in the solid state and leads to high mobility. However, a problem of the linear acene approach is the chemical instability of higher acenes. We thought that the oligomerization of a small acene could also be an effective way to extend a π system.[6,7] Oligo(2,6-anthrylene)s would be interesting because the anthracene monomer itself has high time-of-flight mobility (Scheme 1), and 2,6-substitution is expected to give the most extended π conjugation[8] and the highest planarity.[9] We report herein the synthesis and characterization of 2,2′-bianthryl (**2A**), 2,6-trianthrylene (**3A**), and their dihexyl derivatives (**DH-2A** and **DH-3A**). OFETs with these oligomers have been constructed, and their performances as p-type semiconductors are also presented.

Anthracene oligomers have been synthesized by the Suzuki coupling using palladium catalysts.[10] As shown in Scheme 2, 2-bromoanthracene (**1**) was treated with bis(pina-

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[**] This work was supported by the Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research B 14340226).

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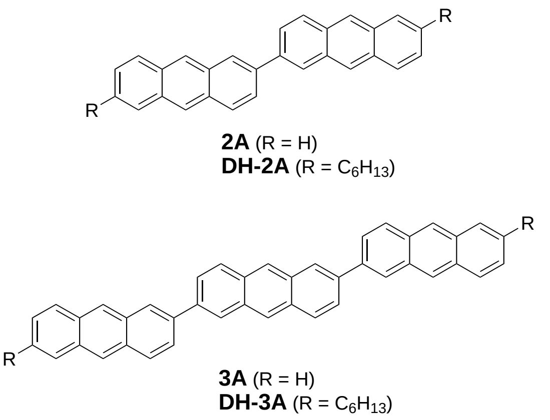
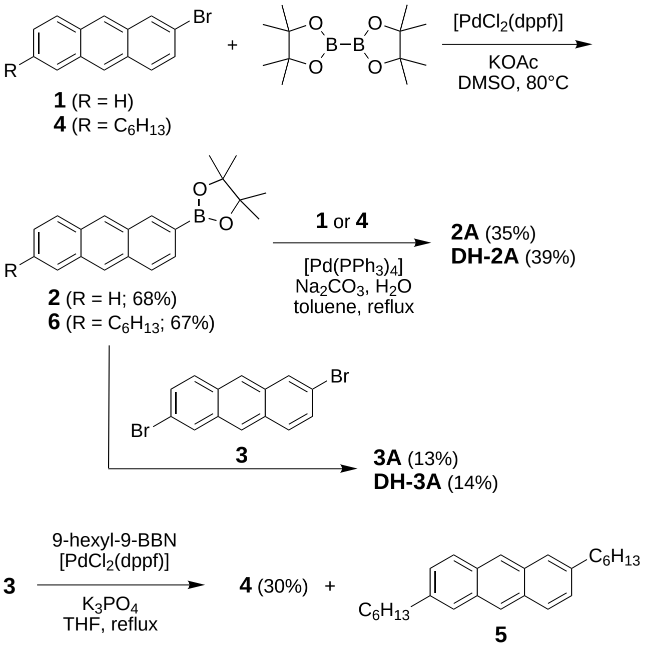


Scheme 1. Structures of anthracene oligomers.



Scheme 2. Synthesis of oligo(2,6-anthrylene)s by Suzuki coupling.

colato)diboron in the presence of [$PdCl_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) to give boronic ester **2** in 68 % yield. The Suzuki coupling of **1** with **2** in the presence of [$Pd(PPh_3)_4$] afforded **2A** in 35 % yield. Similarly, the cross-coupling of 2,6-dibromoanthracene (**3**) with two equivalents of **2** provided **3A** in 13 % yield.[11] An equivalent of 9-hexyl-9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane), which was prepared from 1-hexene and 9-BBN, was allowed to react with **3** in the presence of [$PdCl_2$(dppf)] to give a mixture of 2-bromo-6-hexylanthracene (**4**, 30 %), 2,6-dihexylanthracene (**5**), and **3**. This mixture was converted into boronic esters, and **6** was isolated in pure form (67 %). The Suzuki coupling of **4** with **6** afforded **DH-2A** in 39 % yield. The cross-coupling of **3** with two equivalents of **6** yielded **DH-3A** in 14 % yield.

Anthracene oligomers purified by train sublimation are bright-yellow crystalline solids. Although **2A** and **DH-2A** are slightly soluble in aromatic solvents such as 1,2-dichlorobenzene, **3A** and **DH-3A** are almost insoluble in organic solvents. The structures were determined by mass spectrometry and elemental analyses. Differential scanning calorimetry (DSC) measurements on **2A** and **3A** showed sharp melting endotherms at 374 and 490 °C, respectively.[10] **DH-2A** and **DH-3A** are thermally less stable than the parent compounds and decompose before melting. The dimers (**2A** and **DH-2A**) and the trimers (**3A** and **DH-3A**) exhibit strong blue-green and green photoluminescence, respectively, in the solid state. The emission maxima in chloroform shift to lower energies in the order **2A** > **DH-2A** > **3A** > **DH-3A** (431, 436, 447, and 454 nm, respectively).[12] The electrochemical measurement on **DH-2A** was performed in 1,2-dichlorobenzene. The cyclic voltammogram (CV) showed a quasireversible oxidation at 0.69 V, and the differential pulse voltammogram (DPV) exhibited two oxidation peaks at 0.69 and 0.99 V and a reduction peak at −2.40 V (versus the ferrocene/ferrocenium couple (Fc/Fc^+)).

OFETs of anthracene oligomers were constructed on SiO_2/Si substrates by high-vacuum evaporation at different substrate temperatures using top-contact geometry. The electrical measurements were performed at room temperature. Figure 1 shows the drain current (I_D) versus drain voltage (V_D) characteristics for OFETs with **2A, 3A, DH-2A**, and **DH-3A** at various gate voltages (V_G). FET activity was observed at the substrate temperatures (T_{sub}) between 50 and 70 °C in OFETs with **2A** (Table 1). The hole mobilities calculated in the saturation regime ranged from 0.0031 to 0.013 $cm^2V^{-1}s^{-1}$, and the on/off ratios were 10^3–10^4.[13] The oligomer **3A** showed even higher mobilities (0.031–0.072 $cm^2V^{-1}s^{-1}$) and on/off ratios (10^4–10^5) at T_{sub} = 100–175 °C. The FET performances were dramatically improved when **2A** and **3A** were modified with two hexyl groups:[14] OFETs with **DH-2A** have shown field-effect mobilities greater than 0.1 $cm^2V^{-1}s^{-1}$ at T_{sub} = 70 °C. Although mobilities of **DH-3A** OFETs were lower than those of **3A** OFETs at T_{sub} = 100–150 °C, the highest mobilities (0.14–0.18 $cm^2V^{-1}s^{-1}$) were observed at T_{sub} = 175 °C. These mobilities are still lower than that of pentacene but higher than those of oligothiophenes.[6]

Table 1: FET characteristics of anthracene oligomers fabricated at different substrate temperatures.

Compd	T [°C]	Mobility [$cm^2V^{-1}s^{-1}$]	On/off ratio
2A	50	0.0031	10^3–10^4
	60	0.0088	10^3–10^4
	70	0.013	10^3–10^4
3A	100	0.064	10^5
	125	0.069	10^4
	150	0.072	10^4–10^5
	175	0.031	10^4
DH-2A	70	0.11, 0.13	10^4
	90	0.040	10^4
DH-3A	100	0.027	10^4
	150	0.044	10^4
	175	0.14, 0.18	10^4

Films deposited on Si/SiO_2 substrates were studied by X-ray diffraction in reflection mode at room temperature. Sharp

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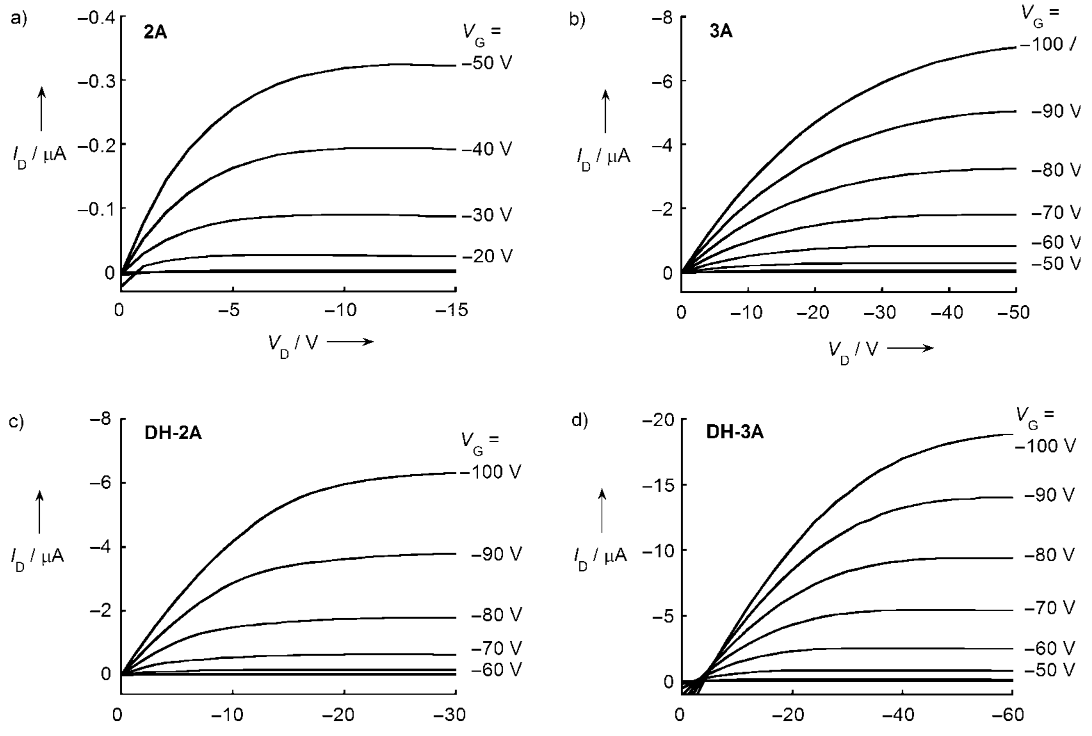

Figure 1. Drain current (I_D) versus drain voltage (V_D) as a function of gate voltage (V_G) for OFETs with anthracene oligomers. a) **2A** ($T_{sub}=70\,°C$); b) **3A** ($T_{sub}=150\,°C$); c) **DH-2A** ($T_{sub}=70\,°C$); d) **DH-3A** ($T_{sub}=175\,°C$). Channel length L: 100 μm; channel width W: 1 mm ($W/L=10$).

and strong reflections up to the sixth order indicated a high degree of lamellar ordering and crystallinity. In the cases of **2A, 3A**, and **DH-2A**, the layer spacings obtained from the first reflection peaks (1.94, 2.84, and 3.20 nm, respectively) correspond to the extended molecular lengths calculated by PM3 (1.83, 2.71, and 3.16 nm, respectively).[15] This result suggests the molecules have a perpendicular orientation on the substrates. Interestingly, the layer spacings of **DH-3A** increase with increasing substrate temperatures during fabrication ($T_{sub}=100\,°C$: 3.52; 150 °C: 3.64; 175 °C: 3.73 nm) and are shorter than the calculated molecular length (3.94 nm). This observation indicates that the molecules are inclined relative to the substrate or there is interdigitation of the hexyl chains.

The field-effect mobilities of anthracene oligomers increased in the order **2A** < **3A** < **DH-2A** < **DH-3A** (0.01, 0.07, 0.13, and 0.18 $cm^2V^{-1}s^{-1}$, respectively). The addition of alkyl groups (from **2A** to **DH-2A**) is more effective than the extension of π conjugation (from **2A** to **3A**).[16] Although the oxidation potential of **DH-2A** (0.69 V) is more positive than that of tetracene (0.52 V versus Fc/Fc^+ in 1,2-dichlorobenzene), the field-effect mobility of **DH-2A** (0.13 $cm^2V^{-}s^{-1}$) is much higher than that of tetracene (0.01 $cm^2V^{-1}s^{-1}$).[4] These results may indicate that the quality of a thin film is more important than the ionization potential of a semiconductor.

In summary, we have shown that the acene–oligomer approach is useful for producing stable p-type organic semiconductors with high field-effect mobilities. The fabrication of OFETs from a solution of **DH-2A** and the synthesis of soluble oligomers based on 9,10-dialkylanthracenes are currently in progress and will be reported elsewhere.

Received: November 12, 2002 [Z50527]

Keywords: biaryls · cross-coupling · oligomerization · semiconductors · thin films

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