SYNTHESIS AND PROPERTIES OF ACENE DIMERS LINKED BY A 1,3,4-OXADIAZOLE SPACER

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Abstract – Acene dimers linked by a 1,3,4-oxadiazole spacer were synthesized and their physical, optical, and electrochemical properties were investigated. The melting points and electron affinities of the dimers increased in the following order: benzene, naphthalene, and anthracene. The longest absorption maximum was red-shifted with an increase in the number of benzene rings. The π-conjugation between the two acene moieties through the oxadiazole spacer was not strong. Although no OFET properties were observed in a bottom contact device using the anthracene dimer as an active layer, the molecules were perpendicularly arranged on the substrate to form π-stacking films as observed in the X-Ray diffraction analysis.

The synthetic research of acene compounds has attracted considerable attention since they are promising materials for the active layers of organic field-effect transistors (OFETs).[1] Pentacene is one of the most useful materials, and it exhibits good p-type semiconducting properties with a mobility of 3 cm^2 V^{-1} s^{-1} and an on/off current ratio of 10^5.[2] Recently, modified acene compounds were also synthesized and their properties were investigated.[3–8] For example, a trimer and dimer of anthracene exhibited good performances as p-type semiconductors with mobilities of 0.07 and 0.01 cm^2 V^{-1} s^{-1}, respectively.[4] The anthracene and tetracene dimers linked by a bithiophene spacer are also p-type semiconductors with mobilities of 0.1 and 0.5 cm^2 V^{-1} s^{-1}, respectively.[5] With regard to this, we synthesized anthracene and

naphthalene dimers (**1**) and (**2**) linked by a 1,3,4-oxadiazole spacer as a new type of modified acene compounds.   Both the acene moieties are expected to be arranged in the form of linear molecular shapes. Further, these compounds are of interest as an approach to n-type semiconductors due to the inherent electron affinity of the oxadiazole moiety, and they were prepared by the condensation of corresponding hydrazides in polyphosphoric acid (PPA).[9]   In this paper, we report the synthesis and properties of these acene dimers together with compound (**3**).
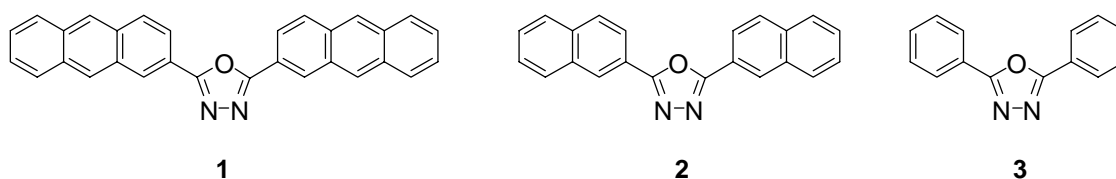
The synthesis of the anthracene dimer (**1**) is shown in Scheme 1.   Methyl 2-anthracenecarboxylate (**6**) was obtained with a yield of 96% by the esterification of carboxylic acid (**5**).   Carbohydrazide (**7**) was prepared with a yield of 88% by the reaction of **6** with hydrazine monohydrate.   The anthracene dimer (**1**) was prepared with a yield of 15% by the condensation of **7** in PPA at 180 °C for 4 h.[10]   A naphthalene dimer (**2**) was obtained by a procedure similar to **1**.[11]   The yields of the condensation, melting points, and color of compounds (**1**)–(**3**) are summarized in Table 1.   The yields of the condensation decreased with an increase in the number of benzene rings in the acene moieties due to the low solubility of carbohydrazide.   The melting point increases with an increase in the number of benzene rings.   The differential scanning calorimetry (DSC) of **1** revealed a melting point of 370.3 °C (T_m) and a crystallization temperature of 332.1 °C (T_c) (Figure 1),[12] suggesting that the anthracene moieties caused a molecular packing with strong intermolecular interactions.   Compound (**1**) was obtained in the form of yellow crystals, which were very slightly soluble in chloroform and dichloromethane and were insoluble in the other common solvents.
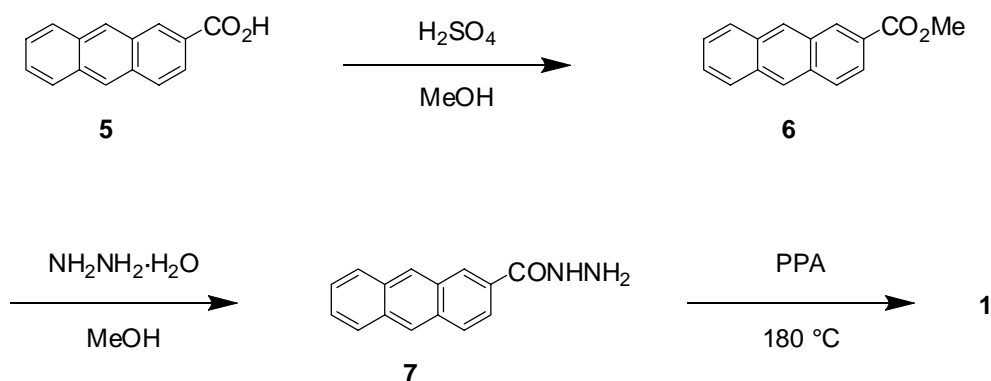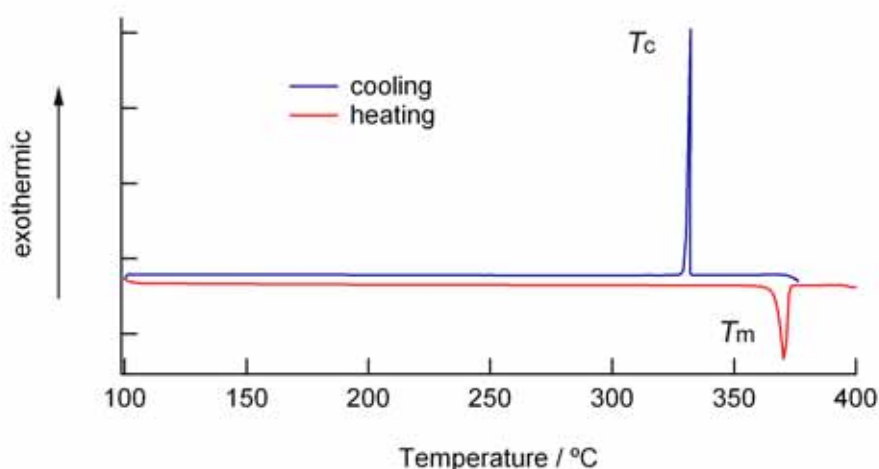

Scheme 1.   Synthesis of anthracene dimer (**1**).

Table 1.   Condensation yields, melting points, and color of **1**–**3**

Compound	Yield / %	mp / °C	color
1	15	370.3[a]	yellow
2	50	194–195	colorless
3	86–92[b]	138–139	colorless

[a]DSC measurement.   [b]Reference 9a.

Figure 1.   DSC profiles of compound (**1**).

The absorption spectra of **1**–**3** in dichloromethane are shown in Figure 2.   The absorption bands are red-shifted with an increase in the number of benzene rings of the acene moieties.   The longest absorption maxima were observed as 281 nm (log ε 4.42) for **3**, 317 nm (log ε 4.51) for **2**, and 402 nm for **1**.   Since the absorption maxima are not much shifted to longer wavelengths as compared to those of benzene (λ_{max} = 254 nm), naphthalene (λ_{max} = 273 nm), and anthracene (λ_{max} = 376 nm), the π-conjugation between the two acene moieties through the oxadiazole spacer appears to be weak.   The HOMO-LUMO energy gaps were evaluated to be 3.77 eV (**3**), 3.35 eV (**2**), and 2.95 V (**1**) according to the absorption edges.   The cyclic voltammetry (CV) of **2** and **3** in DMF revealed reversible reduction waves.[13]   However, the voltammogram of **1** was not recorded because of its insolubility.   The half-wave reduction potentials of **2** and **3** were observed to be −2.28 V and −2.50 V vs. Fc/Fc[+], respectively.   The MNDO-PM3 calculations[14] also indicated that electron affinity increased with an increase in the number of benzene rings in the acene moieties.[15]

A bottom contact OFET was fabricated using compound (**1**) as an active layer with a thickness of 60 nm on a SiO$_2$ (300 nm) dielectric substrate by high vaccum (10^{-5} Pa) deposition. However, the OFET properties were not observed.
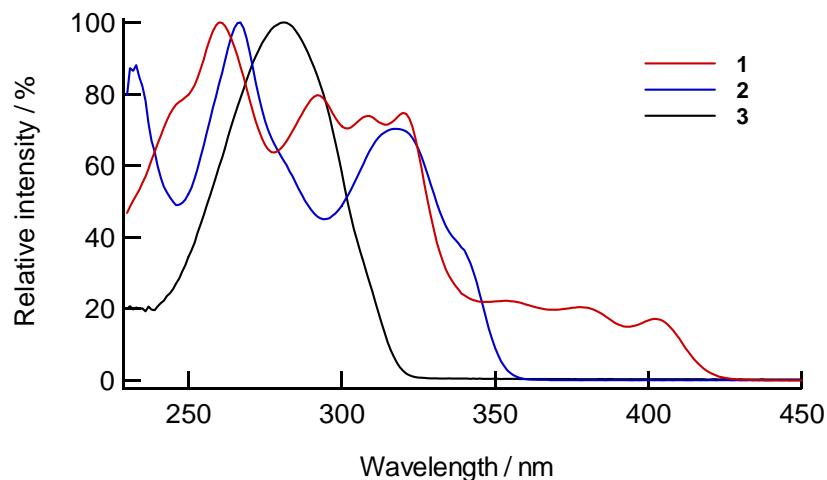
Figure 2.   UV-vis spectra of compounds (**1**)–(**3**) in dichloromethane.

Kwon *et al*. recently reported that molecules of compound (**3**) were arranged horizontally on a Cu(111) surface to form a π-stacking film.   This was observed using scanning tunneling microscopy (STM) and density function theory (DFT).[16]   In order to investigate the thin films of compound (**1**) formed on the SiO_2 substrate, X-Ray diffraction (XRD) analysis was performed (Figure 3).   The XRD profile exhibits sharp diffraction peaks, indicating that these molecules were regularly arranged to form the π-stacking film.   The distance between the molecular layers was calculated to be 2.25 nm from the diffraction peak of $2\theta = 3.92°$.   This distance is comparable to the molecular length calculated by the PM3 method as shown in Figure 4.   Therefore, these molecules were considered to be arranged perpendicularly on the SiO_2 substrate.   This result suggests that no OFET behavior of **1** is not due to the molecular arrangement, but to the insufficient electron affinity.
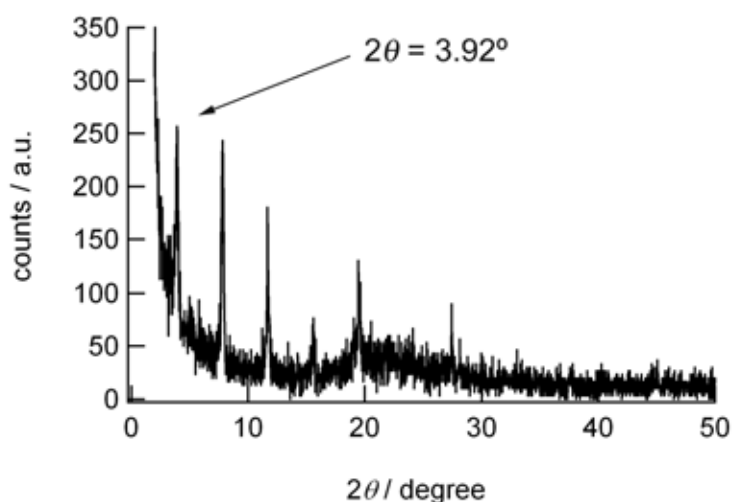

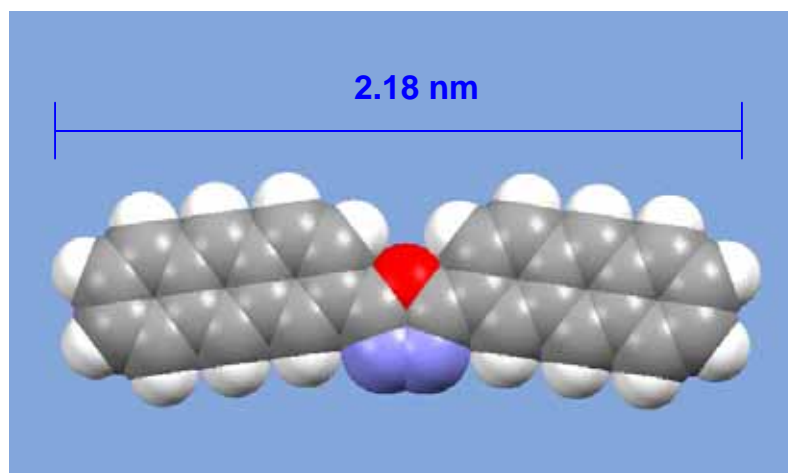**Figure 3.**   XRD of a thin film of **1** formed on a SiO_2 substrate.

Figure 4.   Molecular structure of **1** with the molecular length calculated
by the NMDO-PM3 method.

In conclusion, the preparation of crosslinking acenes by using a 1,3,4-oxadiazole spacer is a useful method for producing modified large acene molecules.   Their physical and electronic properties such as melting point, electron affinity, and HOMO-LUMO energy gap can be turned by changing the acene units. The π-conjugation between the acenes through the oxadiazole spacer was not strong.   According to the XRD measurement and the PM3 calculations, the two acene moieties were arranged to form a linear molecular structure in the thin films.   Although the oxadiazole spacer does not possess sufficient electron affinity, other heterocycle spacers with higher electron affinities may afford new n-type semiconductors.

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10.   Data for compound (**1**): IR (KBr) 3052, 1547, 1456, 1304, 1161, 955, 920, 903, 876, 729, 476 cm^{-1}. Mass (EI, 70 eV) *m/z* (%) 422 (M$^+$, 100), 365 (42), 205 (31), 177 (25).   Anal. Calcd for C$_{30}$H$_{18}$N$_2$O: C, 85.29; H, 4.29; N, 6.63%.   Found: C, 85.03; H, 4.21; N, 6.63%.

11.   Data for compound (**2**): ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.57-7.62 (m, 4H), 7.89-7.92 (m, 2H), 7.98-8.02 (m, 4H), 8.24 (dd, 2H, *J* = 8.5, 1.6 Hz), 8.67 (s, 2H). ^{13}C NMR (50 MHz, CDCl$_3$) δ 121.1, 123.2, 127.1, 127.3, 127.8, 128.0, 128.8, 129.0, 132.8, 134.7, 164.8.   IR (KBr) 1557, 1501, 1001, 829, 752, 482 cm^{-1}.   Mass (EI, 70 eV) *m/z* (%) 322 (M$^+$, 100), 265 (94), 155 (94), 127 (85). Anal. Calcd for C$_{22}$H$_{14}$N$_2$O: C, 81.97; H, 4.38; N, 8.69%.   Found: C, 82.03; H, 4.26; N, 8.63%.

12.   The DSC measurements of **1** were carried out at heating and cooling rates of 10 ºC min^{-1} under nitrogen.

13.   The CV measurements of **2** and **3** were performed in DMF with 0.1 M *n*Bu$_4$NClO$_4$ at a scanning rate of 100 mV s^{-1} using Pt and Ag/Ag$^+$ electrodes.   The values are expressed in potentials vs. Fc/Fc$^+$.

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15.   The MNDO-PM3 calculations indicated that compounds (**1**)–(**3**) have the LUMO energy levels at −1.43, −1.20, and −1.06 eV, respectively.

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