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Synthesis, Crystal Structure, and Physical Properties of 7,14-Disubstituted Pentacene-5,12-diones Containing a Methylenequinoid Structure

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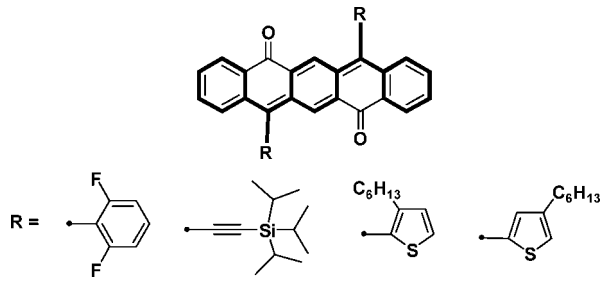
ABSTRACT



Title 7,14-disubsituted pentacene-5,12-diones were prepared for the first time by a nucleophilic substitution reaction of a pentacene-5,7,12,14-tetraone with aryl- or ethynyllithiums followed by a dehydroxylation reaction. The methylenequinoid structures with two conjugated carbonyl groups were clearly observed in their crystal structures. They showed intense absorptions in the visible region and amphoteric redox properties with high reduction potentials.

Extended π-conjugated compounds with quinoid systems have attracted much attention because they have unique electronic states and small HOMO−LUMO energy gaps.[1−3] Methylenequinoid units can serve as useful building blocks to afford electrochemically active compounds. For example, when it is linked with electron-withdrawing groups such as a cyano group, strong electron acceptors, tetracyanoquinodimethane (TCNQ) derivatives, can be obtained. Some of the derivatives show good electron transportation in thin films.[4,5]

On the other hand, fused aromatic compounds with conjugated carbonyl groups are also important candidates for affording n-type semiconductors because the carbonyl groups introduced in the π-systems can strengthen the electron-withdrawing properties leading to facile transportation of electrons.[6] Bearing this in mind, when both the quinoid unit and carbonyl groups are introduced to a π-conjugated compound in a rigid system, the compounds are expected to show novel properties such as high electron affinity in addition to small HOMO−LUMO energy gaps.

In this paper, we have succeeded in preparing such unusual

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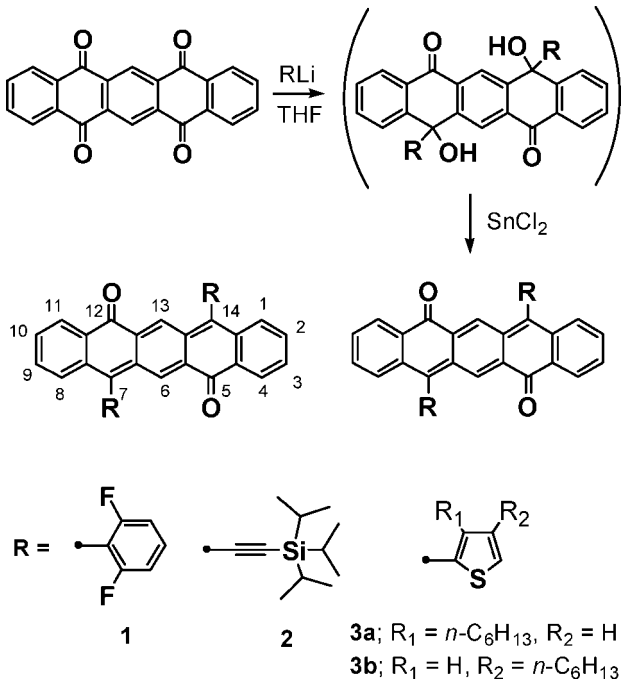
systems. Thus, we have found that 7,14-disubstituted pentacene-5,12-dione derivatives **1**−**3** with a methylenequinoid structure can be simply obtained from a nucleophilic substitution reaction of pentacene-5,7,12,14-tetraones with carbaniones.[7−9] We have used three different types of carbanions like phenyl[7,8] or ethynyl[9] or thienyl anions to prepare the diones and investigated their features and physical properties. We report here the synthesis, structures, intense absorptions and strong electron-withdrawing properties attributed to the methylenequinoid structure.

Scheme 1



A nucleophilic addition reaction of pentacene-5,7,12,14-tetraone with 2.5 equiv of 2,6-difluorophenyllithium, triisopropylsilylethynyllithium (TIPSLi), or thienyllithium afforded the corresponding 7,14-disubstituted diols as shown in Scheme 1. Dehydroxylation reaction using tin(II) chloride under acidic conditions gave 7,14-disubstituted pentacene-5,12-diones **1**−**3** in 52−67% yields. It is noteworthy that even when more than 2 equiv (6 equiv) of 2,6-difluorinated phenyllithium were used, the 7,14-disubstituted diol was obtained as almost a sole product. For the formation of this type of compounds, bulky anions are necessary. Thus, when phenyllithium was used, only a tetrasubstituted derivative was obtained. In the case of thiophene derivatives, alkyl groups were introduced to increase the steric repulsion. While dione **3b** with hexyl groups at the 4-position of the thienyl ring was isolated as a single product in this reaction, **3a** with 3-hexyl groups was obtained as a mixture of rotational regioisomers owing to the restricted free rotation of the C−C bond between the thienyl ring and pentacenedione unit. These compounds were purified by either sublimation or column chromatography. They are stable in both the solid and solution state in air.

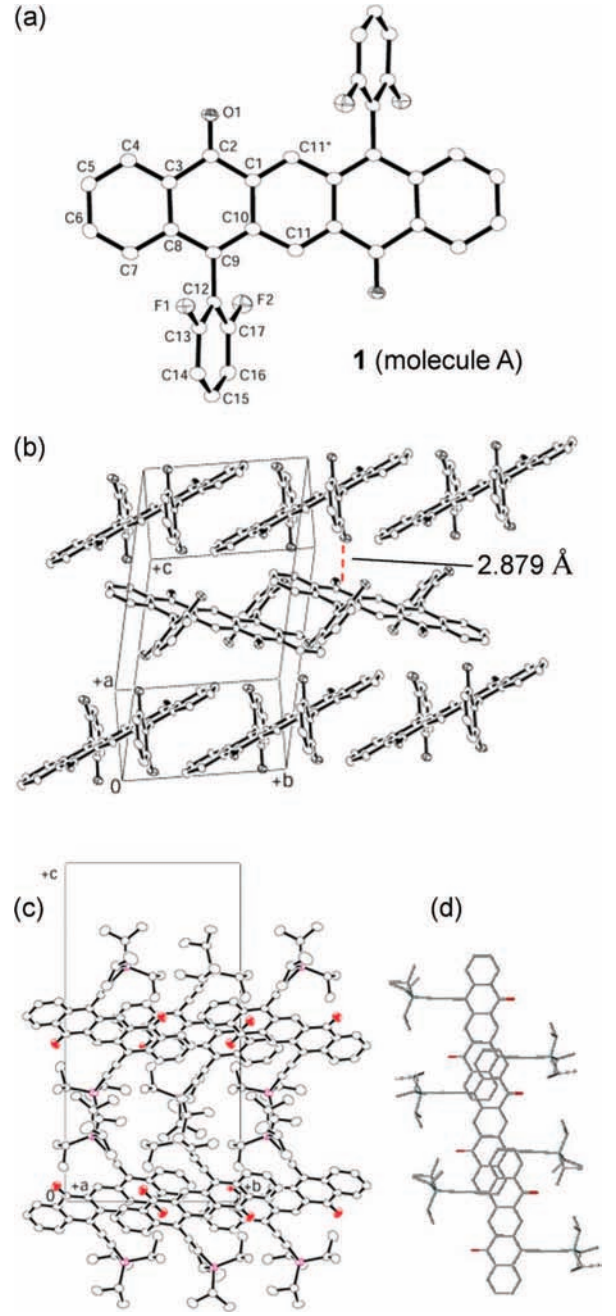


Figure 1. (a) ORTEP drawing of dione **1** containing a methylenequinoid structure. (b) π-Stacking structure of **1** with close F−π contacts. (c) Crystal structure of compound **2**. (d) Overlapping mode of **2**. H atoms are omitted for clarification.

Single crystals of diones **1**−**2** were obtained by slow sublimation. In dione **1**, the pentacene-5,12-dione unit has a planar geometry with a center of symmetry, and the two *ortho*-difluorinated phenyl rings take orthogonal conformation[10] to the planar dione unit affording two crystallographi-

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cally independent molecules with different dihedral angles (63.6° for molecule A and 71.0° for molecule B). In both molecules, the methylenequinoid structures are clearly observed in the central core in Figure 1a, where the C−C bondlengths of C1−C11* (1.363 Å) and C9−C10 (1.384 Å) are shorter than that of C1−C10 (1.454 Å). The two substituents at the 7 and 14 positions can effectively interact with each other in the neutral state. Dione **1** forms a π-staking structure with interplanar distances of 3.588 Å (molecule A) and 3.546 Å (molecule B) with a close intermolecular contact of 2.879 Å between the C atoms of the carbonyl groups and F atoms of the fluorinated phenyl rings. On the other hand, dione **2** containing two TIPS groups also has a planar structure and the central methylenequinoid structure. A one-dimentional π-stacking structure is observed in the crystal with interplanar distances of 3.439 and 3.476 Å as shown in Figure 1d. This stacking structure may be favorable for transporting electrons.

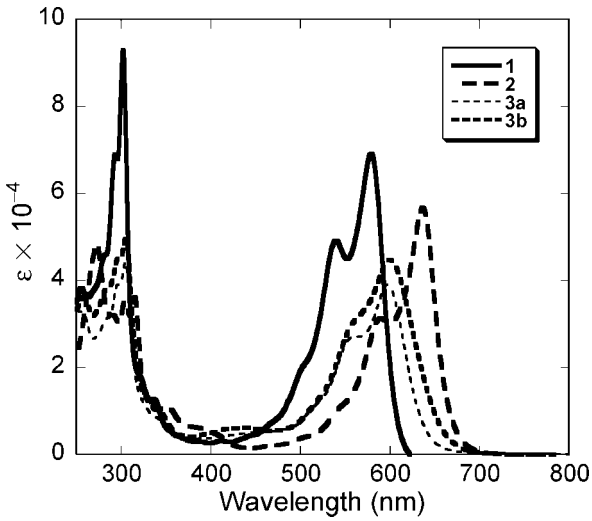

Figure 2. Absorption spectra of compounds **1**−**3** in CH_2Cl_2.

These pentacene-5,12-diones **1**−**3** exhibited intense absorptions in the visible region as shown in Figure 2. The absorption maxima and molar extinction coefficients in dichloromethane are summarized in Table 1. The absorption maximum of dione **1** appears at 578 nm with a large molar extinction coefficient. These intense absorptions in the visible region are considered to be due to charge transfer from the quinoid unit to the carbonyl groups. Introduction of the thienyl rings brings about red-shifts of the absorption maxima to 598 nm in **3a** and 600 nm in **3b**. The TIPS groups in **2** induce a further red-shift of the absorption maximum to 636 nm owing to the extended π-conjugation. The HOMO−LUMO energy gaps were estimated from the end-absorptions and are listed in Table 1. These end-absorptions are somewhat dependent on solvents, thus in polar solvents broad peaks were observed with red-shifts (see the Supporting Information). On the other hand, they showed red fluorescence, whose quantum efficiencies in dichloromethane are shown in Table 1. Among them, dione **1** with orthogonal difluorinated phenyl rings showed the highest efficiency ($\Phi = 0.45$). The solvent effects on the fluorescence spectra were also observed. In ethanol, emission peaks were significantly weakened with red-shifts (see the Supporting Information).

Table 1. Optical Properties[a] of Diones **1**−**3**

dione	λ_{abs} (nm (log ε))	λ_{em} (nm (Φ_f))[b]	λ_{edge} (eV)[c]
1	578 (4.84)	632 (0.45)	1.75
2	636 (4.75)	687 (0.18)	1.61
3a	598 (4.59)	666 (0.01)	1.61
3b	600 (4.65)	*d*	1.58

[a] In CH_2CI_2. [b] Determined by using rhodamine B ($\lambda_{ex} = 535$ nm, $\Phi_f = 0.97$ in EtOH) as standard. [c] Optical HOMO−LUMO gaps determined from the end-absorption in CH_2CI_2. [d] Very weak.

Table 2. Redox Potentials[a] of Diones **1**−**3**

dione	E_{red1} (V)	E_{red2} (V)	E_{pa} (V)
1	−0.28	−0.82	+1.40[b]
2	−0.21	−0.73	+1.24[b]
3a	−0.31	−0.83	+1.32
3b	−0.31	−0.80	+1.06

[a] 0.1 M *n*-Bu_4NPF_6 in DMF, Pt electrode, scanning rate 100 mV s^{-1}, V versus SCE. [b] Determined from differential pulse voltammogram.

These pentacene-5,12-diones **1**−**3** are expected to show amphoteric redox properties with low LUMO levels. The cyclic voltammograms were measured in DMF, and the redox potentials are summarized in Table 2. All compounds **1**−**3** showed two clear reversible reduction waves. The first reduction potential of **1** appeared at −0.27 V, which is significantly high compared to those of indenofluorenediones containing two conjugated carbonyl groups (−0.73 V vs SCE).[11] Introduction of the electron-donating thienyl groups or the acetylene groups did not affect the reduction potentials

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significantly. This result suggests that the reduction potentials are mainly determined by the pentacenedione core. On the other hand, the oxidation peaks were observed as irreversible waves in all of the compounds. The oxidation potentials are more dependent on the substituents at the 7 and 14 positions than the reduction potentials. Thus, the oxidation peak of **3b** with 4-hexyl groups was observed at a lower potential (+1.06 V) than that of **3a** (+1.32 V) with 3-hexyl groups as shown in Figure 3. This may be explained by considering that the thienyl rings in **3b** take a more planar geometry to the core than those in **3a** since the rotational regioisomer of **3b** was not formed. These results suggest that the HOMO levels are dependent on the substituents at the 7,14-positions.

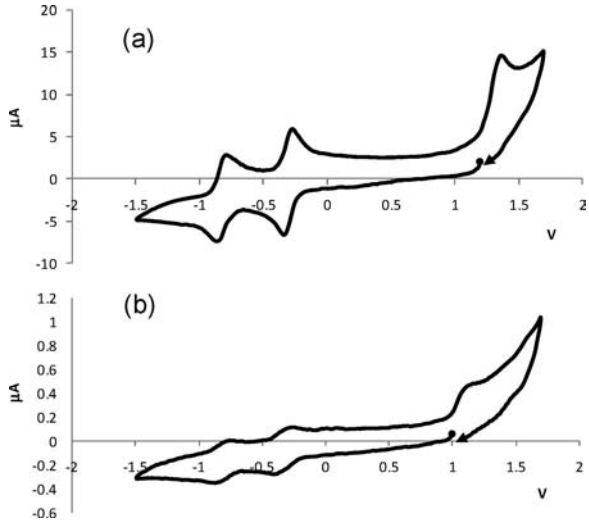

Figure 3. Cyclic voltammograms of compounds (a) **3a** and (b) **3b**.

Carrier mobilities in the films were estimated from the field-effect transistor (FET) measurements. Thin films of diones **1** and **2** were thermally deposited on an SiO_2 dielectric layer with interdigitated Au bottom electrodes at high vacuum (ca. 240 °C for **1** and **2**: 10^{-6} pa).[12] The FET measurements were carried out in situ. The films of **1** and **2** exhibited n-type semiconducting behavior. The electron mobilities (on/off ratio) were calculated to be 1.0×10^{-5} $cm^2V^{-1}s^{-1}$ (150) for **1** and 3.4×10^{-5} $cm^2V^{-1}s^{-1}$ (490) for **2**, respectively.

In conclusion, we have succeeded in preparing 7,14-disubstituted pentacene-5,12-diones possessing a methylenequinoid structure. The methylenequinoid structure combined with carbonyl groups led to strong electron-withdrawing properties and intense absorptions in the visible region. These structures would be useful for novel n-type semiconductors and donor−acceptor type chromophores.[13] The elongation of the π-conjugation by using the terminal positions of thienyl derivatives **3** is currently under way to give new donor−acceptor type compounds applicable for OPVs.[14]

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Supporting Information Available: Detailed experimental procedure, X-ray analysis of **1** and **2**, solvent effects on the optical properties, FET measurements, molecular orbital calculations, and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The SiO_2 (300 nm) surface was treated with hexamethyldisilazane (HMDS) and kept at rt. Threshold voltages were estimated at +13 V for **1** and +6 V for **2**.

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