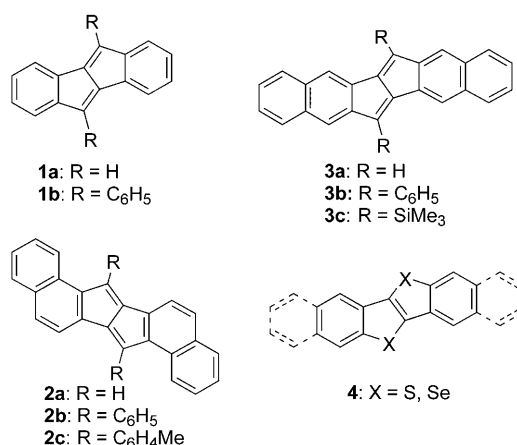


Dinaphthopentalenes: Pentalene Derivatives for Organic Thin-Film Transistors**

Takeshi Kawase,* Takeru Fujiwara, Chitoshi Kitamura, Akihito Konishi, Yasukazu Hirao, Kouzou Matsumoto, Hiroyuki Kurata, Takashi Kubo, Shoji Shinamura, Hiroki Mori, Eigo Miyazaki, and Kazuo Takimiya*

Since the first synthesis of dibenzopentalene **1** by Brand in 1912,^[1a] pentalene derivatives have had a long history of studies on their synthesis, structures, and electronic properties.^[1,2] Recently, polycyclic conjugated systems bearing carbocyclic five-membered rings such as fluorenes^[3] and indenenes^[4] have attracted much attention because of their utility in organic electronic devices. However, the application of pentalene derivatives to organic semiconductor devices has remained underdeveloped to date. Despite possessing a $4n\pi$ -electron periphery, dibenzopentalenes are fairly stable compounds with a planar structure. Thus, appropriate modification would provide them with desirable electronic properties. Last year we found a novel reaction yielding dibenzopentalene derivatives from readily available *o*-bromoethynylbenzenes using commercially available nickel complexes.^[5a] Soon afterwards, Levi and Tilley independently found another efficient dibenzopentalene synthesis using a Pd^0 complex.^[6] These methods would be accessible to various pentalene derivatives.^[5b] In the course of the study, we synthesized di-(1,2)-naphthopentalenes **2** and (2,3)-isomers **3** as entirely new π -extended pentalene derivatives from corresponding bromoethynynaphthalenes. Their electronic and structural properties drastically change with their fusion patterns, which is consistent with theoretical calculations. The structural similarity to dichalcogenophene derivatives **4** as high-performance semiconductors^[7] promoted us to investigate solid-



state properties of **1b**, **2b**, and **3b**. Among them, **3b** showed hole mobility on the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is a very high value for amorphous materials. It is the first pentalene derivative for organic thin-film semiconductors. Furthermore, **3b** was employed as a p-type material for organic heterojunction photovoltaic cells.^[8] Although the power-conversion efficiency (PCE) value (0.94%) is not so high, the open-circuit voltage ($V_{\text{oc}} = 0.96 \text{ V}$) is considerably high.

Treatment of bromoethynynaphthalenes **5** and **6** with a Ni^0 complex,^[9] generated from $[\text{NiCl}_2(\text{PPh}_3)_2]$ and zinc dust in toluene/1,2-dimethoxyethane (DME) (4:1), furnished corresponding dinaphthopentalenes **2b,c** and **3b,c**, respectively, in 11–20% yields (Scheme 1).^[10] Toluene, DME, or THF can be also employed as the solvent, but the yields decreased slightly. Taking into account that three C–C bonds form in one reaction, the yields are not so poor.

The dinaphthopentalenes were obtained as fairly stable crystalline substances. They show different colors: compounds **2** are reddish brown, whereas compounds **3** are orange. Figure 1 shows their absorption spectra in CH_2Cl_2 . In contrast to the fusion pattern, the substituent effects at the 3- and 6-positions are small. The first and second intense absorption bands (250–400 and 400–550 nm) are almost identical to each other. The difference in their colors is due to the presence of the weak, long-wavelength absorption band.

The electronic properties of unsubstituted **2a** and **3a** together with dibenzopentalene **1a** were calculated with the TD-DFT(RB3LYP/6-31G**) calculation embedded in the Gaussian03 software package.^[11] The resultant molecular

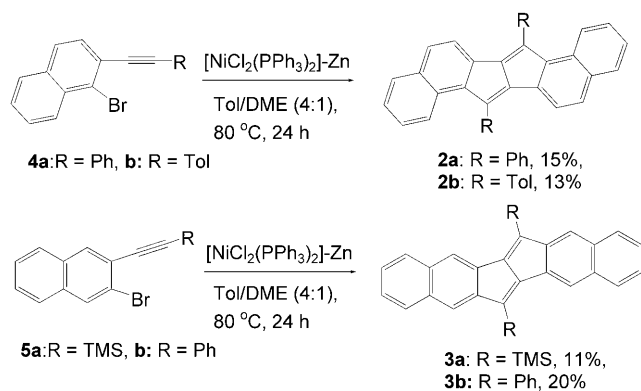
[*] Prof. T. Kawase, T. Fujiwara, Prof. C. Kitamura
Graduate School of Engineering, University of Hyogo
2167 Shosha, Himeji, Hyogo 671-2280 (Japan)
Fax: (+81) 79-267-4889
E-mail: kawase@eng.u-hyogo.ac.jp
Homepage: <http://www.eng.u-hyogo.ac.jp/msc/msc4/index.html>

S. Shinamura, H. Mori, Dr. E. Miyazaki, Prof. K. Takimiya
Graduate School of Engineering, Hiroshima University
Higashi-Hiroshima, Hiroshima, 729-8527 (Japan)
E-mail: ktakimi@hiroshima-u.ac.jp

A. Konishi, Dr. Y. Hirao, Dr. K. Matsumoto, Prof. H. Kurata,
Prof. T. Kubo
Graduate School of Science, Osaka University
1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043 (Japan)

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Scheme 1. Synthesis of **2b,c** and **3b,c**.

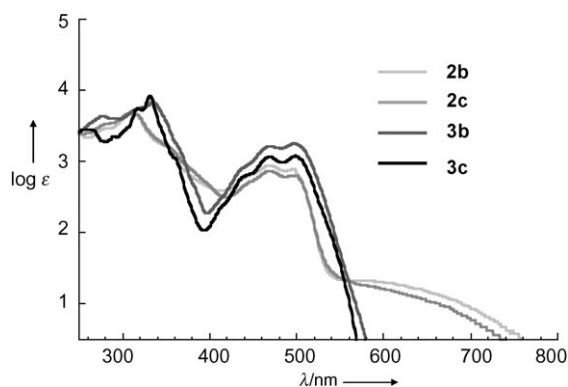


Figure 1. Absorption spectra of **2b,c** and **3b,c** in CH_2Cl_2 .

orbitals and energy diagrams (eV) are shown in Figure 2. The longest absorption bands ($S_0 \rightarrow S_1$ bands) of **2a** are attributable to the HOMO \rightarrow LUMO transitions, which are symmetry-forbidden as is typical for $4n\pi$ -electron systems. In contrast, the calculation of **3a** shows that the HOMO–1 possesses same symmetry as that of the HOMO of **2a**. Thus, the order of the energy levels is reversed by changing the fusion pattern. The TD-DFT calculations also indicate that the longest absorption band of **3a** ($S_0 \rightarrow S_1$ band) is attributable to a HOMO–1 \rightarrow LUMO transition, which is symmetry-forbidden. An allowed HOMO \rightarrow LUMO transition occurs at higher energy, and proximity in energy of HOMO–1 and HOMO would lead to near overlap of the both transitions, which is consistent with the observed absorption spectra of **3**. Conclusively, the HOMO–LUMO gaps of **2a** and **3a** drastically change with the fusion patterns (Figure 2a). The value of **3a** (3.06 eV) is almost comparable to that of **1a** (3.13 eV), whereas the value of **2a** (2.42 eV) is considerably smaller than those of **1a** and **3a**.

Good single crystals of **2b** and **3b** suitable for single-crystal X-ray diffraction studies were obtained from hexane and CH_2Cl_2 /hexane solutions, respectively.^[12] Structural analysis revealed that they have a planar structure (Figure 3). Bond lengths of **2b** and **3b** are summarized in Figure S4a in the Supporting Information. The reported molecular structures of dibenzopentalenes are characterized by large bond alternation in the pentalene moiety and relatively small bond

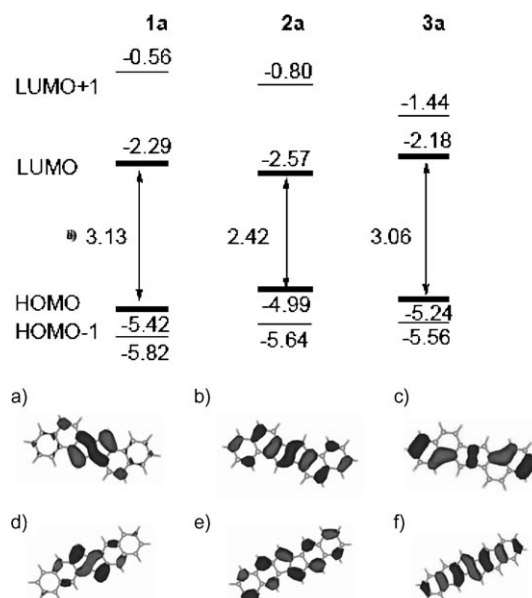


Figure 2. Energy diagrams of **1a–3a** (eV); TD-DFT(RB3LYP/6-31G**) and molecular orbitals of a) LUMO, b) HOMO, and c) HOMO–1 of **2a**, and d) LUMO, e) HOMO, and f) HOMO–1 of **3a**.

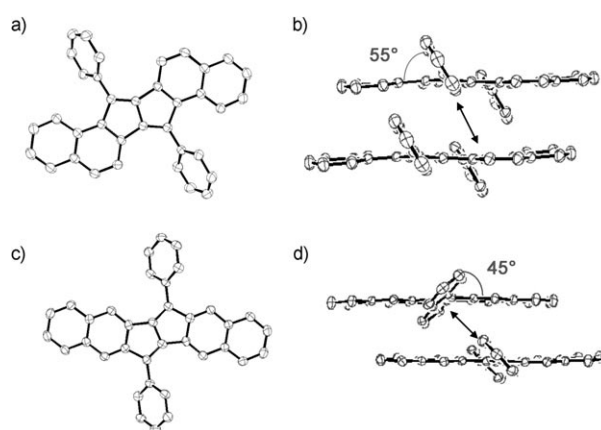


Figure 3. ORTEP drawings (50% probability) of a) top view and b) side view of two molecules of **2b**; c) a top view and d) side view of two molecules of **3b**.

alternation in the six-membered rings. The large bond alternation in the pentalene skeletons of **2b** and **3b** is similar to that of **1b**, and the degrees are largely enhanced. Analogous to **1b**, **3b** possesses *exo*-butadiene conjugations with regard to the pentalene skeleton. The averaged bond length of the 5–6 fusion of **3b** (1.441 Å) is significantly longer than the corresponding one of **1b** (1.425 Å). The longer bond length reflects an unfavorable effect from the $4n\pi$ cyclic conjugation of the pentalene π system. In contrast, the bond length of the 5–6 fusion of **2b** (1.407 Å) is considerably shorter than those of **1a**, which indicate that **2a** possesses a pentalene 8π -electron system. Taking into account a resonance contribution, *exo*-butadiene conjugations with regard to the pentalene skeleton destroy an aromatic sextet in the exterior six-membered rings. In this context, the counterbalance between aromatic stabilization of the exterior

benzene and anti-aromatic destabilization of pentalene π system should determine the bond alternation. These results are also consistent with the predicted bond lengths in optimized structures of **2a** and **3a** (RB3LYP/6-31G**, Figures S1 and S3 in the Supporting Information).

The phenyl substituents of **2b** are tilted 55° from the pentalene plane; the protons of the substituents direct toward the pentalene π plane of neighboring molecules. The resulting CH- π interactions build a slipped parallel stacking arrangement in the crystal. In contrast, two phenyl groups of **3b** direct toward the π plane of the phenyl substituents of neighboring molecules to form a parallel stacking arrangement of the double CH- π interactions; the molecules construct a one-dimensional columnar structure in the crystal (Figure S9 in the Supporting Information).

The redox properties of **2b** and **3b** were examined by cyclic voltammetry. The cyclic voltammograms of **2b** and **3b** exhibit reversible first oxidation and reduction waves for solutions in CH_2Cl_2 (Figure 4), whereas the corresponding dibenzopentalene **1b** shows pseudoreversible oxidation waves under similar conditions. Thus, the extension of conjugation stabilizes their oxidation states. The redox potentials (Table 1) indicate their highly amphoteric redox properties. The electrochemical properties also vary with their fusion pattern; **2b** possesses higher electron-donating and -accepting properties than **3b** and **1b**.

We next investigated the solid-state properties of **2b** and **3b** together with **1b**. These pentalenes readily formed a good thin film on an n-doped Si wafer with 200 nm thermally grown SiO_2 . To obtain information on the film structures, the films

Table 1: Redox potentials of **2b** and **3b** (CH_2Cl_2).^[a]

Compound	$^{\text{ox}}E_{2,1/2}$ [V]	$^{\text{ox}}E_{1,1/2}$ [V]	$^{\text{red}}E_{1,1/2}$ [V]	$^{\text{red}}E_{2,1/2}$ [V]
2b	1.14 ^[b]	0.55	-1.52	-2.06 ^[b]
3b	1.11 ^[b]	0.73	-1.79	-2.26 ^[b]

[a] V vs. Ag/Ag^+ in 0.1 M $n\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$, scan rate 100 mVs^{-1} , 25°C , ferrocene was used as a standard. [b] Peak potentials.

were examined by X-ray diffraction (XRD), which showed no peaks (Figure S5 in the Supporting Information). The results revealed the formation of amorphous films on the surfaces. OFETs were fabricated in a “top-contact” configuration on a heavily doped $n^+\text{-Si}(100)$ wafer with 200 nm thick thermally grown SiO_2 .^[13] The characteristics of the OFET devices were measured at room temperature in air. Whereas **1b** and **2b** showed little mobility under the measured conditions, **3b** had a hole mobility of $1.8 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with current on/off ratio ($I_{\text{on}}/I_{\text{off}}$) of 10^5 at room temperature (Figure 5). The mobility is a very high value for amorphous materials. Takimiya and co-workers reported that the hole mobilities of two structural isomers **7** and **8** were 10^2 to 10^3 times lower than that of **4**.^[14] Higher HOMO energy level of **4** than those of **7** and **8** probably accounted for the difference; however,

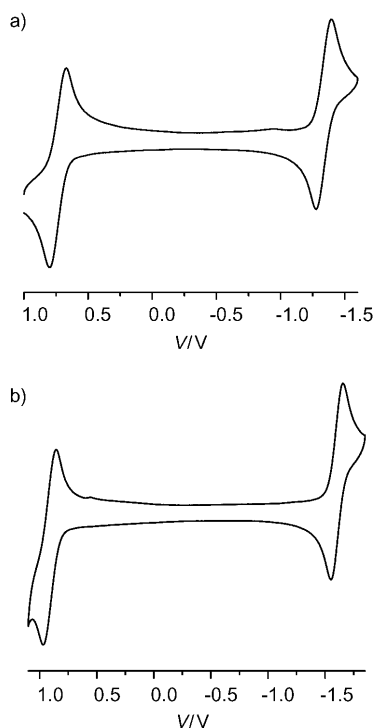
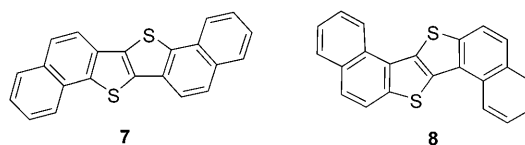


Figure 4. Cyclic voltammograms of a) **2b** and b) **3b** in CH_2Cl_2 (V vs. Ag/Ag^+ in 0.1 M $n\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$, scan rate 100 mVs^{-1} , 25°C ; $\text{Cp}/\text{Cp}^+ = 0.19$ V).

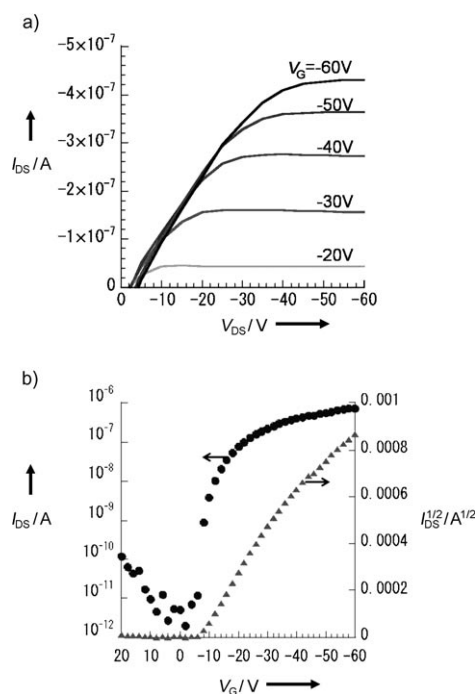


Figure 5. FET characteristics of **3b**-based OFET on OTS-treated substrate at room temperature: a) output characteristics (top) and b) transfer characteristics at $V_{\text{DS}} = -60 \text{ V}$ (bottom). V_{G} = gate voltage, $V_{\text{DS}}/I_{\text{DS}}$ = drain-source voltage/current.

the HOMO energy level of **3b** (−5.44 eV) is lower than that of **2b** (−5.26 eV) and comparable to that of **1b** (−5.52 eV).^[15] These results indicate that the linear fusion pattern in polycyclic conjugated systems plays an important role in the solid-state properties.

Moreover, **3b** was also applied to an electron-donor layer for a heterojunction organic thin-film solar cell.^[16] Fullerene and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were used as an electron-acceptor and an exciton-blocking layers, respectively.^[8] These layers were deposited on the indium–tin oxide (ITO) substrates (see the Supporting Information). The device was fabricated with a structure of ITO/**3b** (40 nm)/C₆₀ (30 nm)/BCP (10 nm)/Al (100 nm) and showed a PCE value of 0.94% and a V_{OC} value of 0.96 V (Figure 6). The PCE value is lower than those of pentacene (2.7%) and tetracene (2.3%). However, the V_{OC} value is considerably higher than those of pentacene (0.58 V) and tetracene (0.36 V), although the conditions were somewhat different.^[17]

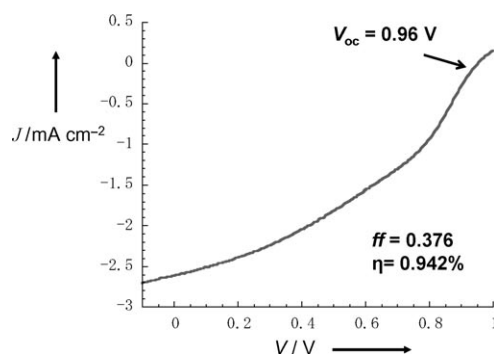


Figure 6. A J – V characteristic for a ITO/**3b**/C₆₀/BCP/Al solar cell device under 100 mW cm^{−2} AM 1.5 G illumination. J = current density, V = bias.

In conclusion, a nickel(0)-mediated reaction of bromoethynynaphthalenes afforded corresponding dinaphthopentalene derivatives as entirely new π -extended pentalene derivatives. The wide applicability to produce a variety of novel π -conjugated systems with pentalene skeletons has been demonstrated. The dependence of the electronic and electrochemical properties upon the fusion patterns is consistent with theoretical calculations. Compound **3b** showed very high hole mobility (1.8×10^{-3} cm² V^{−1} s^{−1}) for an amorphous material, and is thus suitable for organic heterojunction photovoltaic cells; the device showed PCE of 0.94% and a V_{OC} value of 0.96 V. The first pentalene derivative for organic thin-film transistors is now demonstrated. π -Extended pentalenes would serve as a good platform for materials applicable to organic electronics.

Experimental Section

A suspension of bromoethynynaphthalenes (**5** and **6**; 1 mmol), Zn powder (1.5 mmol, 0.098 g), [NiCl₂(PPh₃)₂] (1.0 mmol, 0.654 g) in toluene (4 mL), and DME (1 mL) was heated at 80 °C for 24 h under N₂. The dark reddish reaction mixture was passed through a column

of alumina using hexane/CH₂Cl₂ (1:1) as an eluent to remove insoluble materials. The crude product was then purified by column chromatography on silica gel.

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- [10] See the Supporting Information.
- [11] The molecular geometries of the π -extended pentalenes were fully optimized at the RB3LYP/6-31G** level of theory embedded in the Gaussian03 software package. The time-dependent calculations were performed on the optimized geometries. Theoretical estimation of $S_0 \rightarrow S_1$ absorption bands in **2a** and **3a** were performed with TD-RB3LYP/6-31G**//RB3LYP/6-31G** method.

- [12] Single crystals of **2b** and **3b** for X-ray crystallographic analysis were obtained from *n*-hexane/CH₂Cl₂ and *n*-hexane solutions, respectively. X-ray crystal structure analysis was performed on a Rigaku RAXIS-RAPID imaging plate diffractometer (MoK α radiation, $\lambda = 0.71075$ Å). The structures were solved by direct methods with SHELXS. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by calculation. CCDC 728891 (**2b**) and 728892 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for **2b**: C₃₆H₂₂; $M_r = 454.57$, $a = 14.880(1)$ Å, $b = 4.9221(4)$ Å, $c = 15.904(1)$ Å, $\beta = 95.316(2)^\circ$, $V = 1159.8(2)$ Å³, monoclinic, space group $P2_1/c$, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.74$ cm⁻¹, $T = 200$ K, $D_{\text{calcd}} = 1.302$ g cm⁻³, $F(000) = 476.00$, $R1 = 0.041$, $wR2$ (all data) = 0.109, GOF = 1.07, refl./param. = 10658/649. Crystallographic data for **3b**: C₃₆H₂₂; $M_r = 454.57$, $a = 21.1838(8)$ Å, $b = 9.8827(4)$ Å, $c = 22.7484(9)$ Å, $\beta = 101.7421(1)^\circ$, $V = 4663.1(3)$ Å³, monoclinic, space group $P2_1/c$, $Z = 8$, $\mu(\text{MoK}\alpha) = 0.74$ cm⁻¹, $T = 200$ K, $D_{\text{calcd}} = 1.295$ g cm⁻³, $F(000) = 1904.00$, $R1 = 0.049$, $wR2$ (all data) = 0.227, GOF = 0.68, refl./param. = 10655/649.
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