Organic LETTERS
Letter
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Transition-Metal-Catalyzed Facile Access to 3,11-Dialkylfulminenes for Transistor Applications

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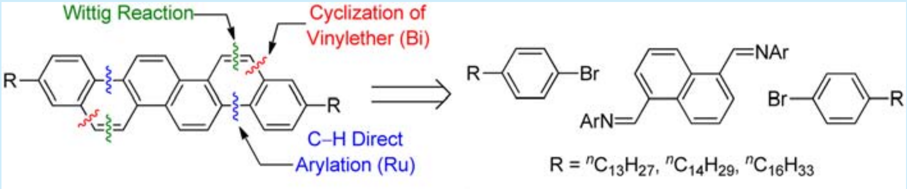
Supporting Information



ABSTRACT: Novel [6]phenacenes (fulminenes) with two long alkyl chains at the axis positions were synthesized. This short synthesis comprises the following three steps: (1) ruthenium-catalyzed direct C−H bond arylation; (2) conversion of directing groups by Wittig reaction; and (3) bismuth- or gold-catalyzed cyclization of vinyl ether. Organic field-effect transistor devices fabricated with a thin film of 3,11-di(tetradecyl)fulminene exhibited typical p-channel normally-off properties.

Organic thin-film field-effect transistors (organic thin-film FETs) have been a subject of much interest due to their potential applications in flexible elecronics.[1] High mobility, low-voltage operation, and air stability, as well as flexibility, are important factors in determining device performance. To fulfill these demands, various polyaromatic hydrocarbons with linear, W-shaped, star-shaped, and butterfly-shaped backbones have been designed and synthesized.[2] Among these, [*n*]phenacenes, in which benzene rings are fused in a W-shaped fashion, have recently attracted much attention[3] because of their higher stability compared with their isostructural analogues [*n*]acenes.

[*n*]Phenacenes represent a novel and promising class of new organic FETs.[4,5] Their performance has improved significantly over recent years, and we have reported that the mobility (μ) reaches 20.9 cm^2 V^{-1} s^{-1}, which is the highest among the p-channel organic thin-film FETs.[6] This value was achieved by [5]phenacene (picene) containing two tetradecyl groups ($^nC_{14}H_{29}$) at the axis positions (3 and 10 positions on the picene backbone). Considering the fact that the μ of picene with no substituents is less than 5 cm^2 V^{-1} s^{-1}, the incorporation of alkyl side chains into other [*n*]phenacene backbones should offer new insights into the development of high performance organic FET devices. Unsubstituted [6]phenacene (fulminene) has been synthesized via condensation followed by aromatization[7a] or oxidative photocyclization.[7b] The synthesis of unsymmetrically substituted fulminenes through (*Z*)-selective hydroboration, Suzuki−Miyaura cross-coupling, and cyclization via direct arylation of the C−H bond was recently reported by Nishihara et al.[7c] The importance of [*n*]phenacenes means the development of efficient alternative routes for the synthesis of suitably functionalized fulminenes directly from simple substrates in fewer steps is an important challenge. This report describes the synthesis and a preliminary mobility study of symmetrical fulminene derivatives with two long linear alkyl chains at the axis positions (3 and 11 positions of the backbone).

Despite numerous studies investigating short transition-metal-catalyzed syntheses of fused-polyaromatic hydrocarbons, its application to the efficient synthesis of [*n*]phenacenes has been limited.[7c,8] We recently reported bismuth-catalyzed cyclization and aromatization of 2-(2-arylphenyl)vinyl ethers leading to various polycyclic aromatic hydrocarbons with phenanthrene backbones.[9] The advantages of this method are the easy availability of cyclization precursors, operational simplicity, and high reaction efficiency. Taking these advantages into consideration, we envisioned that the double cyclization of 1,5-bis(2-methoxyethenyl)-2,6-diarylnaphthalenes would offer an efficient synthesis of 3,11-dialkylfulminenes **1a**−**1c** in a few steps (Figure 1). The formyl groups, which can be utilized to introduce methoxyethenyl groups, would be applicable as directing groups

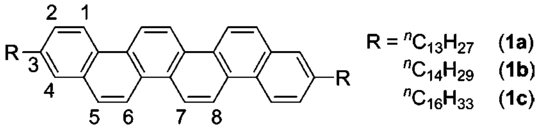


Figure 1. Structure of the target 3,11-dialkylfulminenes **1a**−**1c**.

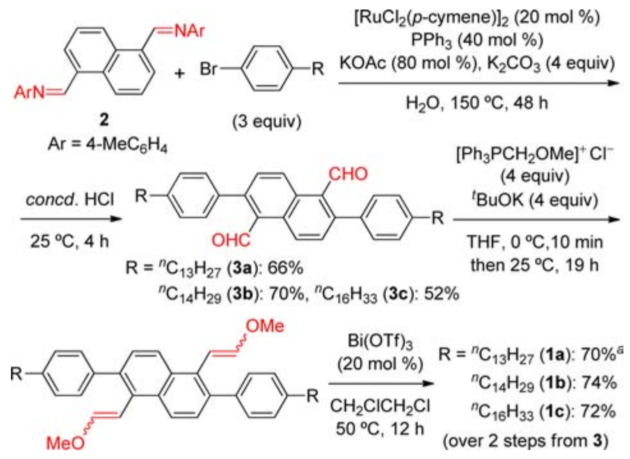
Received: December 26, 2014
Published: January 29, 2015

DOI: 10.1021/ol503723j
Org. Lett. 2015, 17, 708−711

for the construction of multiarylated frameworks by catalytic direct arylation of C−H bonds.

The synthesis began with Ru-catalyzed direct arylation of a C−H bond in aldimine **2**, derived from naphthalene-1,5-dicarboxaldehyde (Scheme 1). This reaction was originally reported by Dixneuf et al. in the synthesis of 1,3-diarylarenes via 2-fold direct arylation of aldimine C−H bonds.[10] The reaction provides an efficient way to construct the 2,6-diarylnaphthalene frameworks of **3a**−**3c** as well as the introduction of formyl groups, which can be easily converted to methoxyethenyl groups by subsequent Wittig reaction with chloro(methoxymethyl)triphenylphosphine. Treatment of regioisomeric mixtures of these vinyl ethers with a catalytic amount of $Bi(OTf)_3$ or $AuCl_3$ furnished the expected 3,11-dialkylfulminenes **1a**−**1c**, respectively, in good yield.[9]

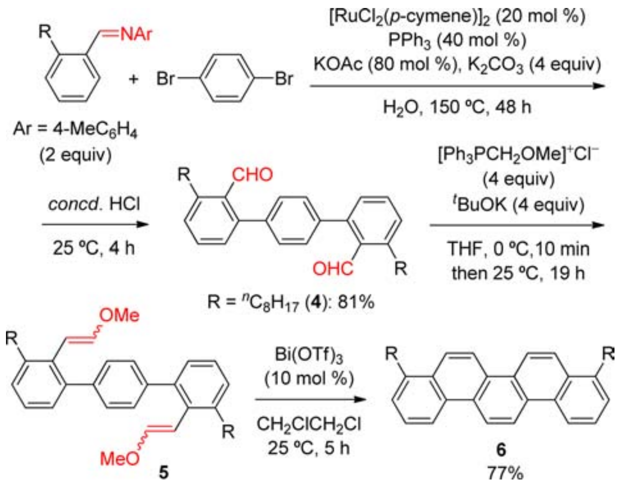
Scheme 1. Synthesis of 3,11-Dialkylfulminenes 1a−1c



[a] $AuCl_3$(10 mol%), 80 °C, 19 h for the second cyclization.

These sequential reactions can be also applied to the construction of other phenacenes, including the dialkylated picene ([5]phenacene)[4a−d] as shown in Scheme 2. In this synthesis, the building blocks used were slightly modified due to the instability of the corresponding aldimine derived from 2-phthalaldehyde. Bismuth-catalyzed cyclization of *p*-terphenyl **5** containing two 2-methoxyethenyl groups, which could be easily prepared via Ru-catalyzed direct arylation of C−H bonds followed by Wittig reaction, afforded 3,10-dioctylpicene **6** in 77% yield.[11] Note that cyclization of **5** proceeded regioselectively to afford picene **6** as a major product, and its regioisomer, dibenz[*a*, *h*] anthracene, was formed in 11% yield (see Table S1 in the Supporting Information (SI) for details).

Scheme 2. Synthesis of 3,10-Dialkylpicene 6



The photophysical properties of 3,11-dialkylfulminenes **1a**−**1c** were investigated by UV−vis absorption spectroscopy to obtain insight into their electronic structures. These compounds showed a maximum peak at 297 nm along with several shoulders in the region of 300−400 nm (Figure S1 in the SI). The lowest transition energies (E_g^{opt}) calculated from the absorption onset are slightly lower than that of the parent unsubstituted fulminene.[7c] These values are summarized in Table 1 along with HOMO energy levels (ionization potential) estimated by photoemission yield spectroscopy (PYS, Figure S2).

Table 1. Optical Data and Energy Levels of Fulminenes

compd	λ_{max}/ nm	λ_{onset}/ nm	E_g^{opt}/ eV[b]	HOMO/ eV[c]	LUMO/ eV[d]
fulminene[a]	293	389	3.19	−5.76	−2.57
1a	297	397	3.12	−5.64	−2.52
1b	297	401	3.09	−5.64	−2.55
1c	297	402	3.08	−5.64	−2.56

[a] Reference 7c. [b] Determined from the onset wavelength in the absorption spectra (E_g^{opt} = $1240/\lambda_{onset}$). [c] Determined by PYS. [d] Determined from HOMO levels and optical bandgaps.

A thin-film FET with 3,10-di(tetradecyl)picene ([5]-phenacene) showed a μ value as high as 20.9 $cm^2 V^{-1} s^{-1}$, which was recorded in our previous study.[6] This μ value is currently the highest among organic FETs. This result stimulated us to try to fabricate an FET device with 3,11-di(tetradecyl)-fulminene ([6]phenacene) **1b**, which is an analogue of 3,10-di(tetradecyl)picene in which only the phenacene core is different. First, in order to determine the nature of **1b**, X-ray diffraction (XRD) was carried out on a polycrystalline powder sample of **1b** at 25 °C. The Le Bail fitting was carried out to determine the lattice constants; the experimental and calculated XRD patterns are shown in Figure 2.[12] Under the Le Bail fitting,

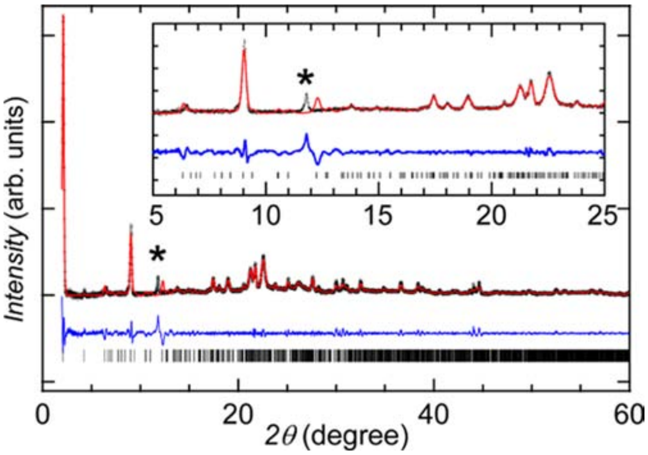


Figure 2. XRD pattern of a powder sample of **1b**. The black dots and the solid red line refer to the experimental and calculated patterns, respectively. The solid blue line refers to the difference between the experimental and calculated patterns. The black sticks represent the predicted positions of Bragg reflection. The asterisk denotes a peak due to impurity.

DOI: 10.1021/ol503723j
Org. Lett. 2015, 17, 708−711

the space group was assumed to be $P2_1$ as in unsubstituted fulminene.[5b] The lattice constants *a*, *b*, *c*, and *β* were determined to be 13.265(2), 5.5707(8), 42.001(5) Å, and 92.50(1)°, respectively. As seen in Figure 2, the pattern calculated using the Le Bail fitting reproduced the experimental XRD pattern well; the weighted pattern *R* factor (R_{wp}) and pattern *R* factor (R_p) were 6.9% and 4.4%, respectively. The van der Waals size of **1b** was estimated to be 50.4 Å, and the average value of $1/|c^*|$, $\langle 1/|c^*|\rangle$, which refers to the distance between the *ab*-plane is determined as 41.3 Å from the XRD pattern; $\boldsymbol{c}^*$ is the reciprocal vector of $\boldsymbol{c}$. Therefore, it was concluded that **1b** inclines by ~35° with respect to the c^* axis. The inclined angle is almost the same as that of unsubstituted fulminene (30°),[5a] suggesting that the addition of long alkyl chains does not have a significant effect on the crystal structure. As expected from the extreme separate ion between the *ab*-planes, channel conductance would occur in the *ab*-plane, as in unsubstituted fulminene.[5a,b]

We characterized a thin film of **1b** based on XRD patterns. Only *001* reflections were observed in the XRD pattern of the thin film (not shown), which means that the *ab*-planes laminate parallel to the SiO_2/Si substrate, which is preferable for transistor application in thin films. The $\langle 1/|c^*|\rangle$ value of the thin film, 41.4 Å, was substantially the same as that of the powder sample, 41.3 Å. The inclined angle of **1b** in the thin film was the same as that of the polycrystalline powder.

An FET device was fabricated using a thin film of **1b**, with a 400 nm thick SiO_2 used as a gate dielectric. The transfer and output curves are shown in Figure 3a and b, respectively. These curves exhibit p-channel normally-off characteristics. The μ, absolute threshold voltage ($|V_{th}|$), on−off ratio, and subthreshold swing (S) were evaluated as 3.2×10^{-1} cm^2 V^{-1} s^{-1}, 13 V, 8.7×10^5, and 2.8 V decade^{-1}, respectively (this device refers to sample 7 in Table S3 in the SI). The μ value is relatively high for organic thin-film FETs, but it is lower by 2 orders of magnitude than that of 3,10-di(tetradecyl)picene, 20.9 cm^2 V^{-1} s^{-1}.[6] The origin of this is not clear, but if it relates to the phenacene core, it should be noted that the symmetry of the picene molecule is different from that of fulminene: the former is C_{2v} and the latter is C_{2h}. This difference may result in a different transfer integral between molecules. Therefore, we must consider the possibility of an even−odd effect of the number of benzene rings on the properties of the FET.[13] This effect may be clarified by investigating the FET properties of dialkyl substituents of more extended phenacene cores. The FET parameters of eight thin-film FETs fabricated using **1b** are listed in Table S3, and the average μ value, $\langle\mu\rangle$, was $3(1) \times 10^{-1}$ cm^2 V^{-1} s^{-1} (Table 2).

Next, we investigated the effect of the number of carbon atoms in the alkyl chain on the properties of the FET in dialkyl substituted fulminene. Thin-film FETs of **1a** and **1c** showed p-channel normally-off FET characteristics, as in the case of **1b**, and the $\langle\mu\rangle$ values were $6(4) \times 10^{-2}$ cm^2 V^{-1} s^{-1} for both **1a** and **1c**, as can be seen from Table 2. The parameters of all FETs fabricated using **1a**−**1c** are listed in Tables S2−S4. Consequently, the $\langle\mu\rangle$ of the thin-film FET composed of **1b** ($3(1) \times 10^{-1}$ cm^2 V^{-1} s^{-1}) is the highest among the 3,11-dialkylfulminenes fabricated in this study, which may imply that the tetradecyl group ($^nC_{14}H_{29}$) effectively provides the fastener effect in molecular packing. If considering both the even−odd and fastener effects, we may expect high μ values for thin-film FETs of [7]phenacenes with two tetradecyl groups.[4e−h]

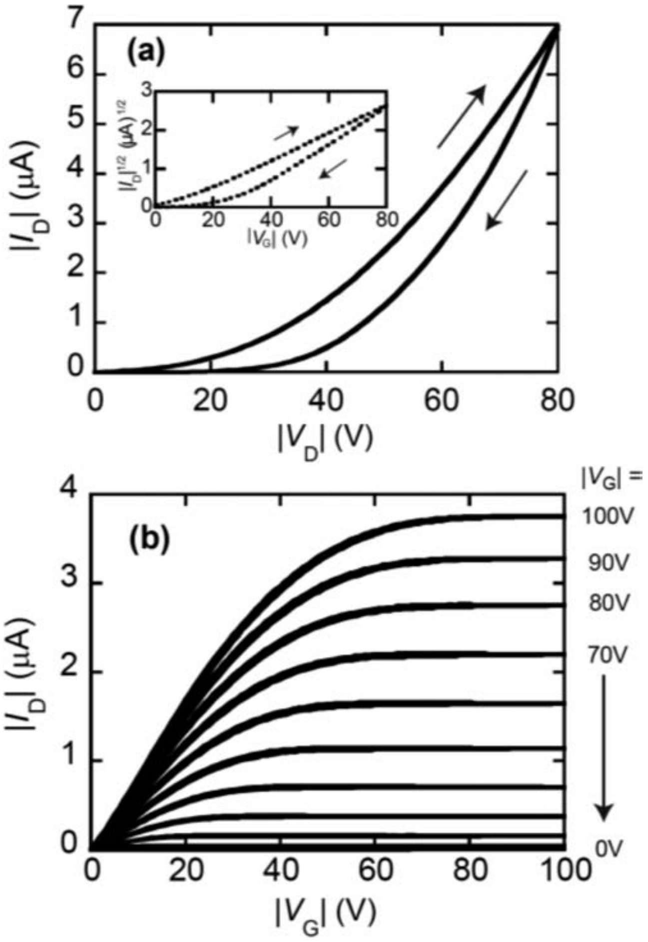


Figure 3. (a) Transfer and (b) output curves for thin-film FET with 3,11-di(tetradecyl)fulminene **1b**.

Table 2. FET Characteristics of 3,11-Dialkylfulminenes Thin-Film FETs with a SiO_2 Dielectric[a]

compd	μ/cm^{2}V^{-1} s^{-1}	$\lvert V_{th}\rvert$/V	on/off	S/V decade^{-1}
1a	$6(4) \times 10^{-2}$	58(7)	$6(6) \times 10^4$	6(2)
1b	$3(1) \times 10^{-1}$	29(11)	$9(8) \times 10^5$	4(2)
1c	$6(4) \times 10^{-2}$	52(6)	$1(2) \times 10^5$	6(3)

[a] All parameters listed refer to the average values evaluated from 6−8 devices (see Tables S2−S4 in the SI for details).

In conclusion, a facile synthetic approach to the construction of novel alkylated fulminenes was demonstrated with the aid of transition-metal-catalyzed transformations. The presence of different alkyl groups ($^nC_{13}H_{27}$, $^nC_{14}H_{29}$, and $^nC_{16}H_{33}$) at 3- and 11-positions did not significantly change their physicochemical properties, but resulted in a dramatic alternation in the FET properties. Only **1b** with two $^nC_{14}H_{29}$ groups showed a high μ value ($\langle\mu\rangle = 3 \times 10^{-1}$ cm^2 V^{-1} s^{-1}), suggesting the presence of a unique fastener effect whereby two $^nC_{14}H_{29}$ groups effectively produce the type of molecular packing that is preferable for channel conductance. However, the μ value was lower by 2 orders of magnitude than that of 3,10-di(tetradecyl)picene, which has the same alkyl groups. Therefore, we suggest that there may be an even−odd effect on the FET properties caused by the different molecular symmetries of picene and fulminene. Because [*n*]phenacenes have attracted considerable attention from the view point of not only their application toward practical FETs[3−6] and oxygen sensors[4a] but also the development of new organic superconductors,[3b] this short synthesis of dialkylfulminenes is expected to contribute significantly to the advancement of organic electronics and materials science. Further studies on the synthesis of new [*n*]phenacenes providing excellent device performance is underway, utilizing molecular design to optimize their optical/electronic properties as well as molecular packing in the crystals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the preparation of compounds and devices, spectroscopic data for all new compounds, copies of ^{1}H and ^{13}C NMR spectra, and thin-film analyses of the materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by a Grant-in-Aid (No. 26248030) from MEXT, Japan, and the Advanced Catalytic Transformation program for Carbon utilization (ACT-C) project of the Japan Science and Technology Agency (JST), and MEXT program for promoting the enhancement of research universities. The authors gratefully thank Mr. Shinji Iba and Mr. Masahiro Nakamura (Okayama University) for HRMS measurements and Takahiro Izumi (Okayama University) for XRD measurement.

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