

Synthesis, Structures, and Properties of Unsymmetrical Heteroacenes Containing Both Pyrrole and Furan Rings

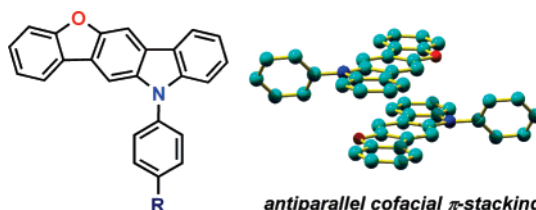
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ABSTRACT



Unsymmetrical heteroacenes, 11-phenylbenzofuro[3,2-*b*]carbazole (Ph-BFC) and its alkoxyated derivatives, were readily synthesized by palladium-catalyzed double *N*-arylation of arylamines. They characteristically form antiparallel cofacial π -stacking arrangements, which may result from their unsymmetrical structures. Their physical properties show their potential for application as active layers in organic field-effect transistors.

The exploration of new organic semiconducting molecules is a crucial topic in organic-based electronic devices such as organic field-effect transistors (OFETs).¹ Recently, intensive research efforts in this field have led to the development of a number of organic semiconductors with high carrier mobilities comparable to those of amorphous silicon.^{2–12}

Among them, pentacene has achieved both an exclusively high hole mobility of $\sim 3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a high on/off ratio of 10^8 .² However, pentacene possesses the disadvantage of undergoing air degradation and/or photooxidation, which poses problems for its practical use in organic devices. Recently, heteroacenes with heteroatoms in fused frameworks, such as thiophene-based dinaphtho[2,3-*b*:2',3'-*f*]-

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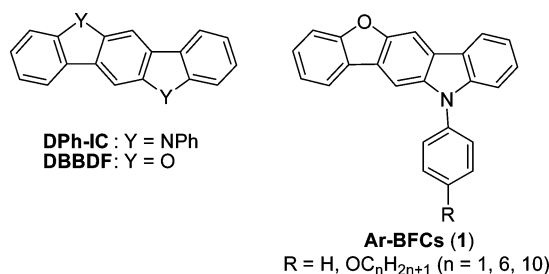
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thieno[3,2-*b*]thiophene (DNTT)^{5d} and pyrrole-based indolo[3,2-*b*]carbazoles (ICs)⁶ have been shown to be promising candidates as hole-transporting materials. OFETs based on these heteroacenes have shown high mobilities ($\mu_{\text{FET}} \approx 2.9 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for DNTT, $\mu_{\text{FET}} \approx 0.2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for ICs) and good environmental stabilities because of their lower HOMO energy levels and larger band gaps than those of pentacene.^{1f,6a} Thus, the development of new heteroacene molecules should be important for the rapid improvement of heteroacene-based OFET materials.

One of the key factors responsible for high electronic performance is the solid-state packing structure.^{7,13–15} In general, strong electronic interactions between the π -electron-rich frameworks of adjacent molecules leads to high charge-carrier mobility. One promising arrangement for strong electronic interaction is a cofacial π -stacking structure. Nuckolls et al. have investigated a series of substituted pentacenes.¹⁵ Among them, a thienyl-substituted compound formed a cofacial π -stacking structure and showed high OFET performance. In contrast, other derivatives with phenyl substituent(s) was packed with the dominant edge-to-face interaction between the pentacene core and the phenyl substituents, that is, without efficient interaction between the pentacene cores, resulting in much lower OFET performance. Anthony et al. also investigated anthradithiophene derivatives with a cofacial arrangement in the solid state, which displayed high OFET performance.^{7b}

In this paper, we report the synthesis of 11-arylbenzofuro[3,2-*b*]carbazole (Ar-BFC), their solid-state structures, and their physical properties. We have recently reported the synthesis of 5,11-diphenylindolo[3,2-*b*]carbazoles (DPh-ICs) and dibenzo[*d,d'*]benzo[1,2-*b*:4,5-*b'*]difurans (DBBDFs) via palladium-catalyzed double *N*-arylation of aniline and intramolecular *O*-arylation, respectively.^{16,17} Photophysical and electrochemical studies of DPh-IC and DBBDF have indicated that DBBDF is more stable than DPh-IC toward photooxidation. Accordingly, we present here a new heteroacene framework based on 11-phenylbenzofuro[3,2-*b*]carbazole (Ph-BFC) as a molecule with enhanced environmental stability compared to DPh-IC. Unlike DPh-IC and DBBDF, the crystal structures of Ar-BFCs show antiparallel cofacial π -stacking arrangements between heteroacene cores, which are expected to cause significant orbital interaction.

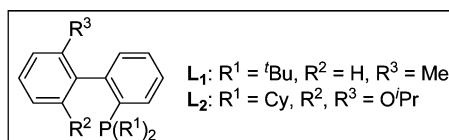
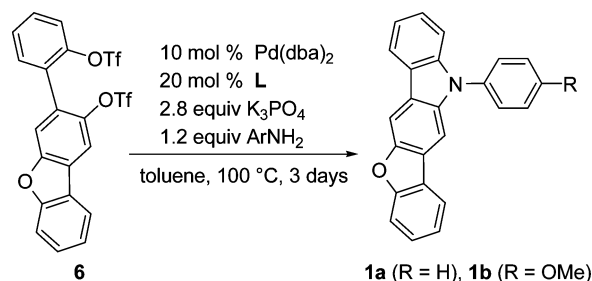


The synthesis of BFCs was conducted with palladium-catalyzed double *N*-arylation as a key reaction (Table 1).¹⁷

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Table 1. Synthesis of Ar-BFC **1** by Double *N*-Arylation of Aniline with **6**

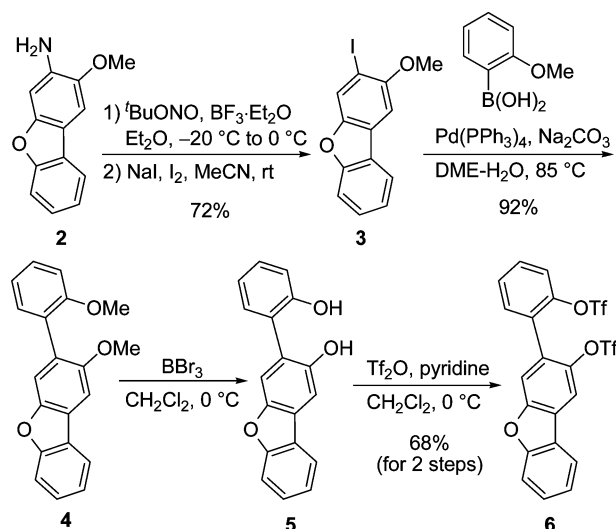


entry	ligand	R	yield of 1 (%)
1	L ₁	H	60
2	L ₂	H	67
3	L ₂	H	97 ^a
4	L ₂	OMe	72

^a Use of 15 mol % of Pd(dba)₂ and 30 mol % of **L**₂.

First, the substrate for the double *N*-arylation was synthesized as shown in Scheme 1. Commercially available 3-amino-2-

Scheme 1. Synthesis of Bistriflate **6**



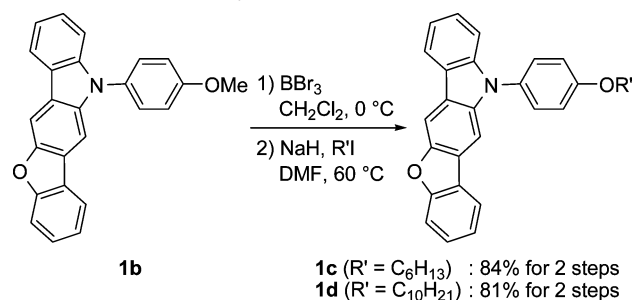
methoxydibenzofuran **2** was converted into iodide **3** via the Sandmeyer reaction (72%). The following Suzuki–Miyaura cross-coupling reaction with 2-methoxyphenylboronic acid produced a 92% yield of **4**. Demethylation of **4** and

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subsequent esterification with triflic anhydride produced a 68% yield of bistriflate **6** (2 steps). The double *N*-arylation of aniline with **6** was initially examined in the presence of Pd(dba)₂ (10 mol %), ligand **L**₁¹⁸ or **L**₂¹⁹ (20 mol %), and K₃PO₄ (2.8 equiv) in toluene at 100 °C (Table 1). The use of ligand **L**₂ resulted in a slightly higher yield of the desired **1a** (67%) than that using ligand **L**₁ (60%) (entries 1 and 2). A small amount of **5** was observed as a byproduct in both reactions, which would be produced via the hydrolysis of bistriflate **6**. Optimally, a 97% yield of **1a** was obtained when using 15 mol % of the palladium catalyst (entry 3). The coupling of **6** with *p*-anisidine was also successful, resulting in a 72% yield of **1b** (10 mol % Pd) (entry 4). Methoxy-substituted Ar–BFC **1b** is a useful platform for further transformation. Thus, alkoxyated derivatives **1c** and **1d** were obtained via demethylation of **1b** and subsequent alkylation with the corresponding iodoalkanes (Scheme 2). All

Scheme 2. Synthesis of Ar–BFCs **1c** and **1d**



Ar–BFCs dissolved in common organic solvents such as CHCl₃, THF, and toluene. Therefore, they were purified via silica-gel column chromatography and characterized by ¹H and ¹³C NMR spectroscopy and HRMS.

The solid-state ordering of **1a**, as determined by single-crystal X-ray crystallography, is shown in Figure 1a. As described in our previous report,¹⁶ DBBDF showed a molecular ordering dominated by edge-to-face interactions between heteroacene cores, leading to a herringbone arrangement. DPh–IC also formed dominant edge-to-face interactions in the solid state. However, the two pendant phenyl groups on the nitrogen atoms of DPh–IC caused weaker interaction between the heteroacene cores. In sharp contrast, the solid-state ordering of **1a** is completely different from that of DBBDF and DPh–IC. Two molecules form a pair with cofacial and antiparallel stacking (Figure 1a). Such a stacking structure is probably due to the steric effect of the unsymmetrically placed phenyl group. A small molecular dipole moment of **1a** may also contribute to such an antiparallel

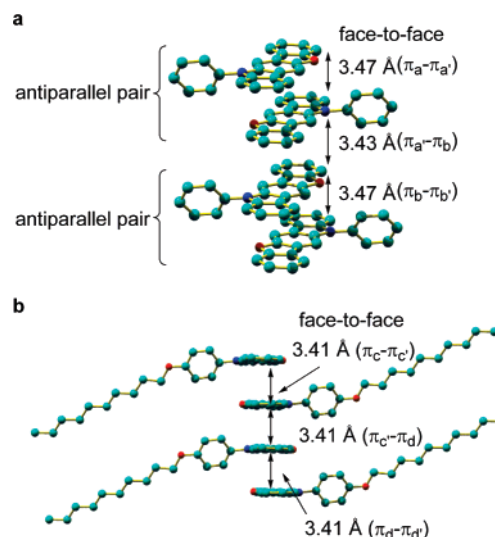


Figure 1. Solid-state orderings of Ar–BFCs (a) **1a** and (b) **1d**.

arrangement.²⁰ The antiparallel pairs further stack in a cofacial manner, resulting in a one-dimensional stacking column. The interplanar π -stacking distance between two molecules in the same stacked pair (π_a – $\pi_{a'}$, π_b – $\pi_{b'}$: 3.47 Å) is slightly greater than that between different pairs ($\pi_{a'}$ – π_b : 3.43 Å). The pendant phenyl group is inclined at approximately 57.4° with respect to the acene plane. One phenyl group also has an edge-to-face interaction with the acene core (C_π – C_{ph} : 3.61, 3.80 Å) and the phenyl groups (C_{ph} – C_{ph} : 3.67 Å) in neighboring columns (Figure S1, Supporting Information). Single-crystal structures of **1c** and **1d** were also obtained, and the molecular arrangement was found to be very similar between the two (Figure S2 for **1c**; Figures 1b and S3 for **1d**; see Supporting Information). Similar to **1a**, two molecules of **1d** form a cofacial and antiparallel pair, and the pairs further stack in a cofacial manner to form a π -stacked one-dimensional column. Alkyl side-chains interdigitate, giving a lamellar structure (Figure S3, Supporting Information). The interplanar π -stacking distances between two molecules in the same pair (π_c – $\pi_{c'}$, π_d – $\pi_{d'}$) and between different pairs ($\pi_{c'}$ – π_d) are the same (3.41 Å). One phenyl group has an edge-to-face interaction with the acene core in neighboring columns (C_π – C_{ph} : 3.48 Å) (Figure S3, Supporting Information). Compared to **1a**, both the cofacial and the edge-to-face distances are slightly shorter. The closer packing structure may be due to the self-assembly property of long alkyl chains.

The photophysical and electrochemical data of Ar–BFCs are summarized in Figure 2 and Table 2. As shown in the UV/vis spectra, the absorption maximum of **1a** is slightly blue-shifted compared to that of DPh–IC and red-shifted compared to that of DBBDF. The HOMO–LUMO energy band gap of **1a** (E_{g-1a}), as evaluated from an absorption edge ($\lambda = 393$ nm), is 3.15 eV, which is larger than $E_{g-DPh-IC}$

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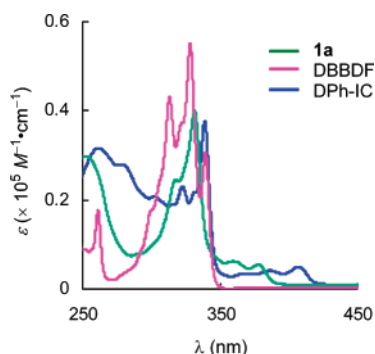


Figure 2. UV/vis spectra of **1a**, DPh-IC, and DBBDF in CHCl_3 (1×10^{-5} M).

and smaller than $E_{\text{g-DBBDF}}$. Cyclic voltammetry experiments of parent Ph-BFC **1a** (Figure S4, Supporting Information) show one reversible oxidation wave in the scan range of 0–1.5 V, in contrast to DBBDF, which produces one quasi-reversible wave, and DPh-IC, which produces two reversible waves.¹⁶ The HOMO energy level of **1a** ($E_{\text{HOMO-1a}}$), as evaluated from the first oxidation onset ($E_{\text{ox onset}}$), is 5.59 eV below the vacuum level. $E_{\text{HOMO-1a}}$ is between $E_{\text{HOMO-DPh-IC}}$ and $E_{\text{HOMO-DBBDF}}$, indicating that Ph-BFC **1a** is less sensitive to oxidative degradation than DPh-IC. The LUMO energy level of **1a** ($E_{\text{LUMO-1a}}$) is –2.44 eV, which is lower than $E_{\text{LUMO-DPh-IC}}$ and $E_{\text{LUMO-DBBDF}}$. These experimentally estimated energy levels of the frontier orbitals of **1a** are consistent with those obtained from MO calculations (see

Table 2. Photophysical and Electrochemical Data of Heteroacenes

compound	λ_{edge} (nm) ^a	E_{g} (eV) ^b	$E_{\text{ox peak}}$ (V)	$E_{\text{ox onset}}$ (V) ^c	E_{HOMO} (eV) ^d	E_{LUMO} (eV) ^e
1a	393	3.15	1.17	1.01	–5.59	–2.44
1c	395	3.14	1.03	0.90	–5.48	–2.34
1d	395	3.14	1.10	0.95	–5.53	–2.39
DPh-IC ^f	422	2.95	0.67	0.46	–5.08	–2.13
			1.24			
DBBDF ^f	354	3.50	1.59	1.16	–5.78	–2.28

^a Absorption edge. ^b Determined from the absorption edge. ^c Onset potentials (vs Ag/Ag^+) of first oxidation wave determined by cyclic voltammetry: 0.1 M Bu_4NClO_4 in CH_2Cl_2 , Pt as working and counter electrodes, scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$. ^d Calculated according to $E_{\text{HOMO}} = -e(E_{\text{ox onset}} + 4.58)$. ^e All values were estimated from the optical band gaps and E_{HOMO} . ^f See ref 16.

Supporting Information). The alkoxy substituents on the phenyl group have little effect on the photophysical properties of the molecules (Table 2, Figure S5, Supporting Information),²¹ whereas they do affect the electrochemical properties; HOMO and LUMO levels of the alkoxy derivatives **1c** and **1d** were found to be higher than those of parent **1a** (Table 2 and Figure S4).

In summary, we report the synthesis of Ar-BFCs—unsymmetrical heteroacenes containing both nitrogen and oxygen atoms—via palladium-catalyzed double *N*-arylation of arylamines with dibenzofuran precursor **6**. Ar-BFCs are soluble in common organic solvents and exhibit an antiparallel cofacial π -stacking structure in the solid state, which would cause strong electronic coupling. Such a π -stacking pattern presumably results from their unsymmetrical structures. Thus, the present molecular design of the unsymmetrical introduction of a substituent on a (hetero)acene core would provide a guide to a cofacial arrangement of the (hetero)acene core. Photophysical and electrochemical experiments suggest that BFCs should be expected to possess high oxidative stability. Further studies on the synthesis of a series of BFCs as well as their application to OFETs are now in progress in our laboratory.

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Supporting Information Available: Experimental procedures, solid-state orderings, cyclic voltammograms of **1a**, **1c**, and **1d**, UV/vis spectra in solutions (**1a–1d**) and in thin films (**1c** and **1d**), ^1H and ^{13}C NMR spectra for synthesized compounds, and crystallographic information files for **1a**, **1c**, and **1d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) The UV/vis spectra of **1c** and **1d** in thin films can be found in the Supporting Information.