



Palladium-catalyzed carbonylative annulation toward new [1,2,5]thiadiazole-fused heteroacenes for solution-processed field-effect transistors

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ABSTRACT

A straightforward synthetic strategy toward [1,2,5]thiadiazole-fused heteroacenes via the Pd-catalyzed carbonylative (PdCC) annulation utilizing the building blocks of 5,6-substituted benzo[2,1,3-*b*]thiadiazole (BT) and 1 atm CO has been successfully developed. Preliminarily, solution-processed Field-effect transistor (FET) devices based on **FTCS** exhibited a promising mobility up to 0.177 cm²/(Vs) with a current on/off ratio of nearly 1.2×10^5 under an ambient atmosphere. This chemistry opens new perspectives toward high performance heteroacenes.

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Acenes are a class of aromatic hydrocarbons composed of linearly fused benzene rings, which have already shown potential applications in organic electronics such as organic field-effect transistors.¹ Since the remarkable performance of pentacene in high performance OFETs was discovered,^{1b} numerous efforts have been devoted to the design and synthesis of extended π -conjugated systems with planarity and rigidity, i.e., larger linear acenes.² The state-of-the-art charge carrier mobilities for thin film OFETs are 19.3 cm²/(Vs) in the case of vacuum-deposited acenes³ and 31.3 cm²/(Vs) for solution-processed heteroacenes.⁴ This impressive accomplishment is mainly achieved by the molecular engineering of the structures of acene-based semiconductors.^{2,5} However, the chemistry of polyacenes always involves multiple synthetic steps and tedious purifications,⁶ which deeply restricted the realization of their usage in OFET devices.

Palladium-catalyzed carbonylative (PdCC) coupling reactions of aromatic halides and related compounds have attracted increasing attention during recent years,⁷ due to their versatile applications in

synthesis of ketones, alkynones, chalcones, etc.^{8–10} These compounds have been widely used as important intermediates for pharmaceuticals, agrochemicals, and other industrial products, but few have been used in organic semiconducting materials. Very recently, the synthetic routes to various substituted fluoren-9-ones have been developed via an efficient PdCC multiple C–C bond formation method.¹¹ These works indicate significant efforts should be paid to exploiting organic π -conjugated system via PdCC strategy (Fig. 1).

Mobility enhancement and environmental robustness to oxidation in ambient air are two major requirements of organic semiconductors for OFETs.¹ The general approaches to achieve stable polyacenes with desirable bandgaps and energy levels include introducing extensive functional groups onto the acene core to provide both steric and electronic protection^{1b} and/or replacement carbon atoms within π -system by other atoms (e.g. imine nitrogen⁵ or sulfur^{2c}). Recently, the electron-deficient heterocycle of thiadiazole has been used to afford 1,2,5-thiadiazole-fused compounds,¹² because this ring leads to several advantages such as a high electron affinity, no steric repulsion between the adjacent aromatic rings, and strong intra/intermolecular interaction caused by short S...N contacts. However, few of

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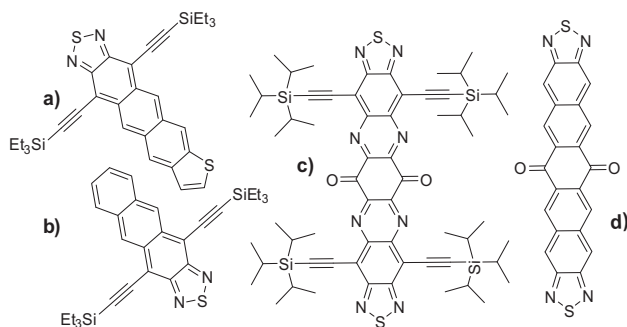


Figure 1. chemical structures of [1,2,5]thiadiazole-fused heteroacenes.

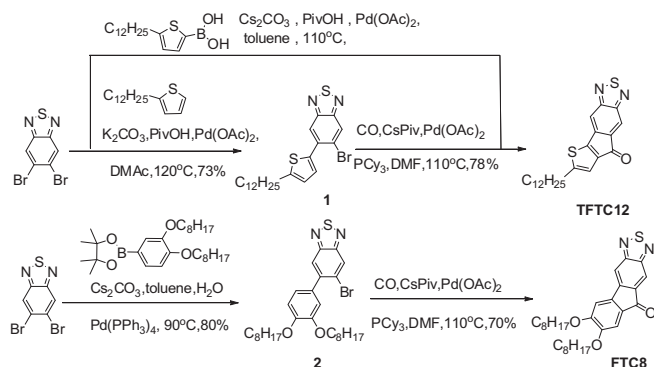
them can be used as active materials for OFETs by the low-cost solution-processed techniques. In this regard, we report the straightforward synthetic strategy toward [1,2,5]thiadiazole-fused heteroacenes **TFTC12** and **FTC8** via coupling and subsequent Pd-catalyzed carbonylative annulation utilizing the building blocks of 5,6-substituted benzo[2,1,3-b]thiadiazole (BT) (Scheme 1). The target molecules can also be considered as BT-embedded heteroacenes with different side-chains for tuning their solubility and aggregation behavior in solid state.^{1c} In addition, lower-lying HOMO/LUMO levels were expected for these compounds, because both the electron-deficient ketone and [1,2,5]thiadiazole groups were combined in the molecular backbone.

The synthetic route of the [1,2,5]thiadiazole-fused heteroacenes **TFTC12** and **FTC8** is depicted in Scheme 1. 5,6-Dibromobenzothiadiazole (5,6-DBrBT) was readily available according to the reported protocol with optimization.¹³ Firstly, we tried the Pd-catalyzed carbonylative multiple C–C formation in ‘one-pot’ fashion¹⁰ with 5,6-DBrBT and 5-dodecyl-2-thienyl boronic acid as the starting materials, but they afforded **TFTC12** at very low yields of 20–27%. Then, we moved to the two-step strategy. The key intermediates **1** and **2** were prepared through direct C–H arylation coupling¹⁴ and Suzuki coupling, respectively. Compound **1** can also be prepared through Suzuki coupling of 5-dodecyl-2-thienyl boronic acid and 5,6-DBrBT in 35–40% yields, but the direct C–H arylation of 2-dodecylthiophene and 5,6-DBrBT is superior in good yield of 73%. It was assumed that under direct C–H arylation conditions the reactivity of bromine atom was restricted after the other Br was replaced by dodecylthiophene. When 5,6-DBrBT and 3,4-bis(octyloxy)-1-phenyl boronic ester were subjected to Suzuki coupling in 1:1.3 mole ratio, **2** can be obtained in high yield of 80%. At this moment, the PdCC coupling reaction worked very well by transforming **1** to **TFTC12** and **2** to **FTC8** in yields of 78% and 70%, respectively. All new compounds can be isolated with silica column chromatography and their chemical structures can be

unambiguously identified with nuclear magnetic resonance (NMR) spectra and mass spectra due to their good solubility in common organic solvents. **TFTC12** and **FTC8** exhibited good thermal stabilities by losing less than 5% of weight upon being heated up to 330 °C in N₂ as determined by thermogravimetric analysis (TGA) (Figs. S9 and S10). **TFTC12** shows two endothermal peaks at 85 °C (*T_g*) and 109 °C (melting point, mp), corresponding to exothermal peaks at 83 °C and 61 °C (Fig. S11) as determined by differential scanning calorimetry (DSC). Compound **FTC8** shows endothermal peaks at 177.1 °C and exothermal peak at 155.2 °C (Fig. S12). Thermal induced phase transition results indicate both compounds are crystalline materials, implying their potentials as OFET active layers.

The UV–vis absorption spectra of **TFTC12** and **FTC8** were recorded in dilute solutions (1×10^{-5} M) in dichloromethane and in thin films. In dilute solution, **FTC12** exhibited a strong π – π^* transition with a maximum absorption at ca. 296 nm and a weak charge transfer band at 383 nm, respectively (Fig. 2). Vibronic bands for the absorption bands of **TFTC12** were observed, which arose from the enhanced rigidity in its chemical structure. Interestingly, **FTC8** showed another weak shoulder absorption band at 443 nm except for the π – π^* transition band (278, 318 nm) and the charge transfer band (370 nm). UV–vis absorption spectra of **TFTC12** and **FTC8** in thin films showed red-shifted and broader absorption bands in comparison with those in dilute solutions, which indicates the existence of improved solid-state packing. Additionally, the absorption spectra in films show no vibronic bands, due to aggregation induced intermolecular frontier orbital hybridization. From the long wavelength absorption bands in dilute solutions, the optical energy gaps (*E_{opt g}*) are calculated to be 2.63 and 2.42 eV for **TFTC12** and **FTC8**, respectively (Table S1).

Time-dependent density function theory (TD-DFT) calculations (B3LYP/6-311G*) were conducted to elucidate the absorption spectra of **TFTC12** and **FTC8**. As predicted by the calculations, both **TFTC12** and **FTC8** show intense absorptions at ca. 294 nm, but only **FTC8** shows a weak absorption at the longer wavelength with the maximum at 447 nm (oscillator strength $f = 0.0714$) (Table S4), which is mainly attributed to the transition from HOMO to LUMO. This small oscillator strength is consistent with the low absorption intensity.¹⁵ Importantly, the whole shape of the absorption spectra and the tendency agree well with the experimental results. The frontier molecular orbital (FMO) profiles of **TFTC12** and **FTC8** indicate that both of the two molecules are planar and adopt spatially separated HOMO and LUMO levels (Fig. 3), which results in the formation of intramolecular donor–acceptor structures. It is therefore reasonable that [1,2,5]thiadiazole serves as the electron acceptor



Scheme 1. Synthesis of **TFTC12** and **FTC8**.

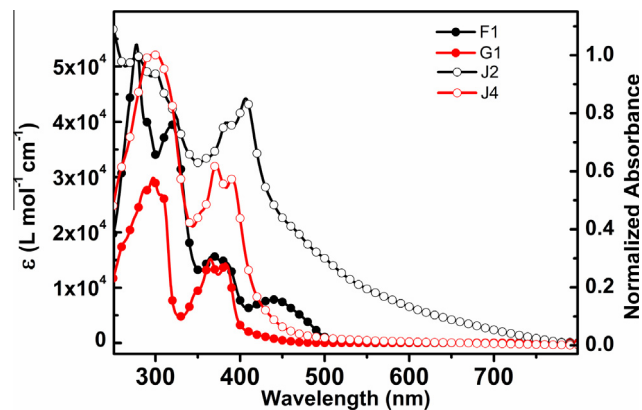


Figure 2. UV–vis absorption spectra of **TFTC12** and **FTC8** (recorded in 1×10^{-5} M CH₂Cl₂ solution, and in spin-coated film on quartz with 10 mg/mL chloroform solution).

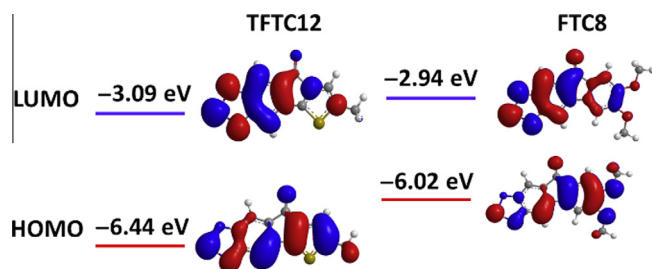


Figure 3. DFT (B3LYP/6-311G*) calculated frontier molecular orbital energies and surface topologies of **TFTC12** and **FTC8**.

and alkyloxybenzene (**FTC8**)/thiophene (**TFTC12**) ring serves as the electron donor, leading to intramolecular charge transfer (ICT) transition. The calculated HOMO and LUMO levels are shown in Figure 3.

To better understand their energy levels and bandgaps, the electrochemical properties of compounds **TFTC12** and **FTC8** were investigated by cyclic voltammogram (CV) (Fig. 4). Compound **TFTC12** exhibited quasi-reversible oxidation wave with onset potential (E_{ox} onset) at 1.70 V and reversible reduction wave with onset potential (E_{red} onset) at -0.65 V, corresponding to HOMO and LUMO levels of -6.13 eV and -3.78 eV, respectively. Interestingly, **TFTC12** exhibited reversible oxidation wave with E_{ox} onset = 1.42 V and quasi-reversible reduction wave with E_{red} onset = -0.74 V, corresponding to HOMO and LUMO levels of -5.85 and -3.69 eV, respectively. The oxidation potentials of **TFTC12** and **FTC8** are much higher than those of tetracene and pentacene, suggesting their stability against oxygen oxidation in air. The trend of electrochemical bandgaps (2.35 eV for **TFTC12** and 2.16 eV for **FTC8**) is in good agreement with that of the optical bandgaps deduced from their absorption spectra in dilute solutions and those obtained from theoretical simulations.

OFET devices based on **FTC8** and **TFTC12** were fabricated and evaluated via solution-processed method.¹⁶ However, attempts to fabricate FET devices using **TFTC12** unfortunately failed. All the devices did not show FET characteristics owing to its low mp. The transistors based on **FTC8** were found to exhibit typical *p*-type FET characteristics in air. In the pristine films, the transistors of **FTC8** exhibit a hole mobility up to $0.03 \text{ cm}^2/(\text{Vs})$, with a current on/off ratio of 1.07×10^6 (Table S5). After thermal annealing at 120°C for 5 min in N_2 atmosphere, the FET performance was

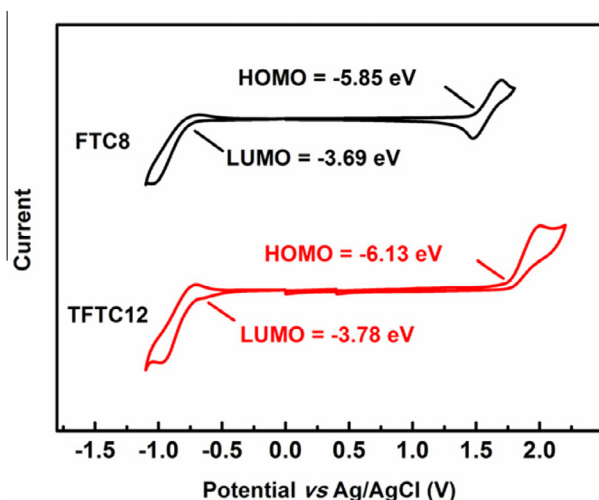


Figure 4. Cyclic voltammograms of compounds **TFTC12** and **FTC8** in dry CH_2Cl_2 .

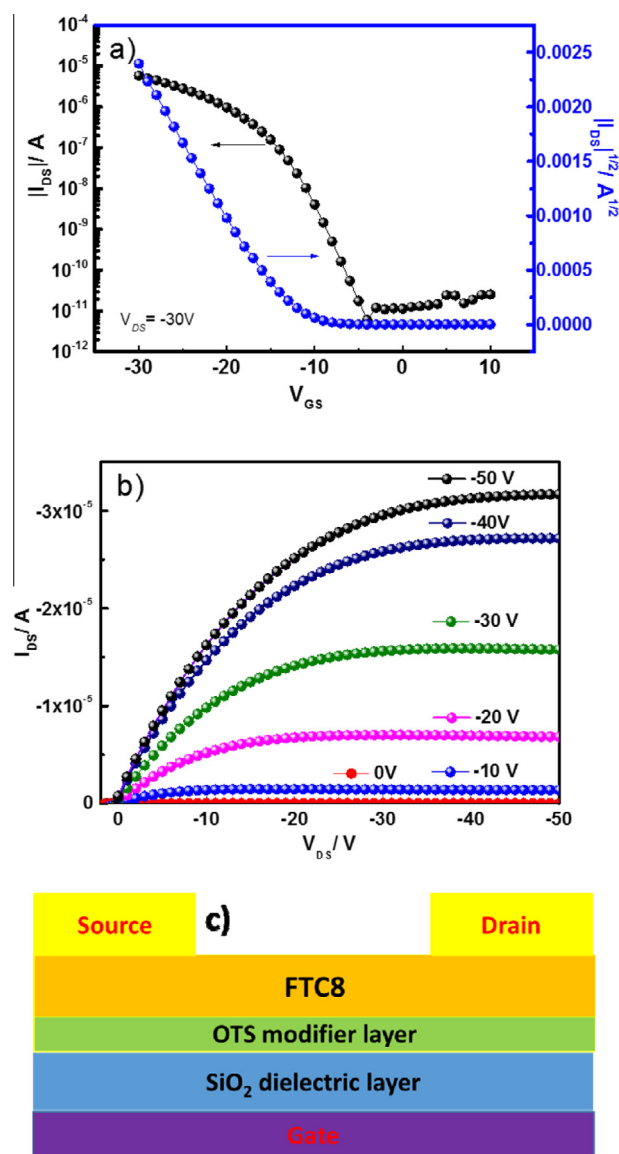


Figure 5. Typical (a) transfer and (b) output characteristics of FETs based on **FTC8** (thermal annealing at 120°C for 5 min in N_2), and (c) OFET device geometry.

enhanced by achieving a hole mobility up to $0.177 \text{ cm}^2/(\text{Vs})$, threshold voltage $V_{th} = -10.4 \text{ V}$ and a current on/off ratio of 1.2×10^5 . Typical transfer and output characteristics of the OFET devices based on **FTC8** are shown in Figure 5a and b, respectively.

In summary, we have successfully established practical synthesis of [1,2,5]thiadiazole-fused heteroarenes with soluble side-chains via Pd-catalyzed carbonylative annulation protocol. Physicochemical investigation of obtained heteroarenes revealed their potential as organic semiconductors. Preliminarily, solution-processed FET devices based on **FTC8** exhibited a promising mobility up to $0.177 \text{ cm}^2/(\text{Vs})$ with a current on/off ratio of nearly 1.2×10^5 under an ambient atmosphere. Further investigations to develop new materials via this protocol are now actively being conducted in our research group.

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Supplementary data

Materials and experimental details, NMR spectra, MALDI-TOF MS spectra, UV–vis absorption spectra, TGA, DSC and CV curves, DFT data and other transfer/output curves of **FTC8**. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2016.07.008>.

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