

Phase Tag-Assisted Synthesis of Benzo[*b*]carbazole End-Capped Oligothiophenes

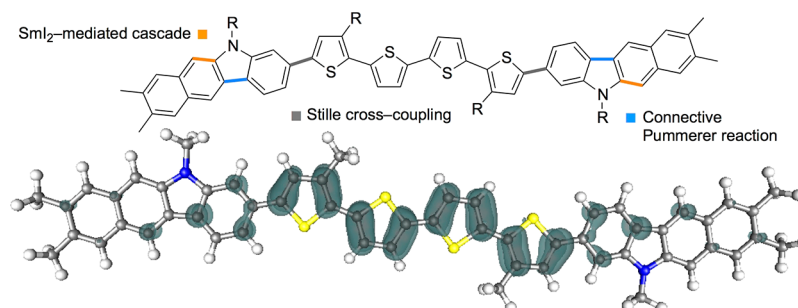
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Received October 5, 2012

ABSTRACT



The introduction and removal of a phase tag have been used to trigger cyclization events in a new synthesis of benzo[*b*]carbazoles. The approach has been exploited in a tag-assisted approach to new benzo[*b*]carbazole end-capped oligothiophenes for preliminary evaluation as semiconductors.

The development of tagging strategies¹ continues to play a key role in the quest for more efficient synthesis. The use of a phase tag usually introduces two synthetically redundant steps to a sequence: tag introduction and tag removal. In recent years, we have explored new strategies that allow a higher synthetic return to be gained from the unavoidable steps during which the tag is introduced and removed.² We have focused on the development of processes in which tag introduction and removal trigger key cyclization events, with the ultimate goal of developing efficient tag-assisted syntheses in which tag introduction–cyclization and tag

removal–cyclization operate alongside established tag-assisted purification technologies. We recently described the first applications of such an approach in the synthesis of the natural product neocryptolepine^{2e} and in the synthesis of a library of spirooxindole natural product analogues for biological evaluation.^{2f} Herein, we report a phase tag-assisted approach in which tag introduction and tag removal trigger cyclization events en route to benzo[*b*]carbazole end caps, which have been used to prepare novel oligothiophenes for evaluation as organic semiconductors (Scheme 1).

Extensive effort has been invested in the discovery of new organic semiconducting materials, and the optimization and understanding of their performance.³ Much of this interest has been driven by the unique advantages offered by organic semiconductors relative to their inorganic counterparts. In particular, organic semiconductors have the potential for low-cost, large-area device fabrication on flexible substrates. Organic semiconductors can be

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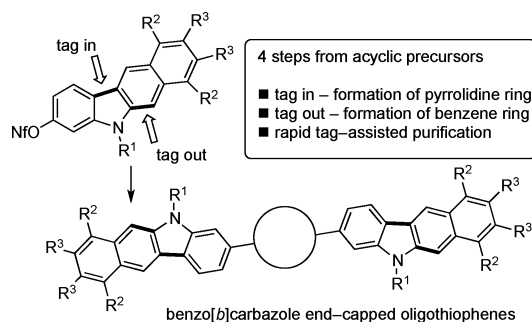
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Scheme 1. Phase Tag-Assisted Approach to End-Capped Oligothiophenes^a



^a Circle represents a thiophene-based linker.

either molecular or polymeric in nature. Oligothiophenes are the most well studied molecular materials.⁴ In particular, acene end-capped oligothiophenes have been shown to be promising organic semiconductors for applications in organic field effect transistors (OFETs).⁵ Field effect mobilities and $I_{\text{on/off}}$ values up to $0.40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 1×10^5 have been reported for devices fabricated using vacuum evaporation.^{5a} Devices made by solution processing show slightly lower values at $3.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 4.5×10^4 , respectively.^{5b} In this Letter we describe the construction of novel benzo[b]carbazole end-capped oligothiophenes using tag introduction–cyclization and tag removal–cyclization strategies alongside tag-assisted purification technologies and detail their preliminary evaluation as organic semiconductors.

We have previously reported a tag introduction–cyclization process^{2a,b} based on a connective Pummerer-type reaction⁶ that allows a fluorous tag⁷ to be introduced and a heterocycle to be constructed in a one-pot reaction. With the fluorous tag in place, fluorous solid-phase extraction (FSPE)⁸ can be used to purify intermediates without recourse to conventional purification methods.

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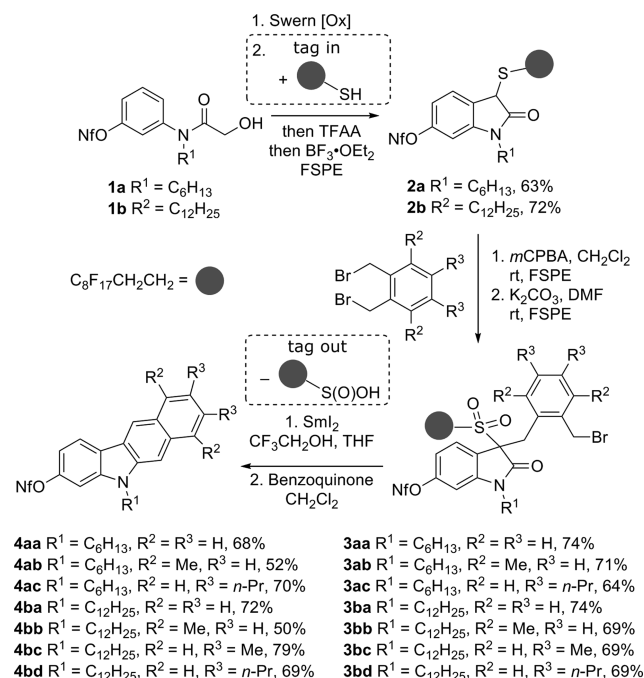
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FSPE involves filtration through commercial fluorous silica gel, washing first with a fluorophobic solvent mix, to remove untagged impurities, and then a fluorophilic solvent mix, to isolate the tagged product. Tagged oxindoles **2a,b** were prepared using a modification of our Pummerer⁹ approach and were purified conveniently using FSPE. With the nonaflate group on the aromatic ring in amides **1a,b**, good regiocontrol was observed in the Pummerer cyclization and **2a,b** were obtained as a separable 4:1 mixture of isomers in favor of the desired isomer shown. Subsequent oxidation and alkylation with a range of 1,2-bromomethylbenzenes gave sulfones **3aa–3bd** after purification using FSPE after each stage (Scheme 2). FSPE proved particularly valuable for the isolation of intermediates **3** as they were unstable to conventional flash chromatography.

Scheme 2. Phase Tag Introduction–Cyclization and Phase Tag Removal–Cyclization in a Fluorous Synthesis of Benzo[b]carbazoles



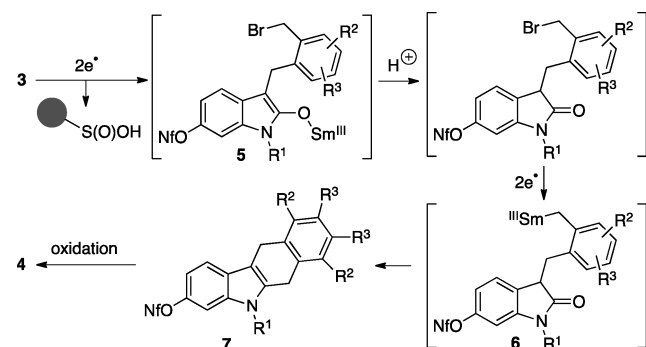
Pleasingly, treatment of sulfones **3aa–3bd** with the electron transfer reductant samarium(II) iodide (SmI_2)¹⁰

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triggered tag removal¹¹—cyclization to give carbazoles **4aa–4bd** in good overall yield after oxidation of the crude product mixture using benzoquinone. The tag removal—cyclization step constitutes a new approach to benzo[*b*]carbazoles and proceeds by the generation and protonation of samarium(III) enolate **5**,¹² followed by the formation and Barbier cyclization of benzylic organo-samarium(III) intermediate **6**.¹³ Oxidation of the crude cycloadducts **7** then gave benzo[*b*]carbazole products (Scheme 3).

Scheme 3. Mechanism of Phase Tag Removal—Cyclization: A New Approach to Benzo[*b*]carbazoles



The benzo[*b*]carbazoles prepared by our tag-assisted approach can be used to generate solution-processable end-capped oligothiophenes **9a–j** by efficient Stille cross-coupling¹⁴ with thienyl tributyltin coupling partners **8a–e** (see Supporting Information for the structures of **8a–e** and details of their preparation) (Figure 1). The optical and electrochemical properties of the end-capped oligothiophenes were examined by UV–vis absorption spectroscopy, fluorimetry, and cyclic voltammetry. Cyclic voltammetry was undertaken using spin coated thin films on platinum foil as the working electrode and Ag/AgNO₃ as a reference electrode in MeCN solution containing 0.1 M TBAPF₆ as a supporting electrolyte.

The redox behavior was referenced against ferrocene (Fc) as an internal standard, and HOMO energy levels were then calculated using the equation E_{HOMO} (eV) = $(-4.8 - E_{\text{onset}} + E_{1/2}[\text{Fc}])$. Representative CV curves (for **9a**, **9e**, and **9i**) are shown in Figure 2. The estimated HOMO levels all lie in the range -5.0 to -5.4 eV, which

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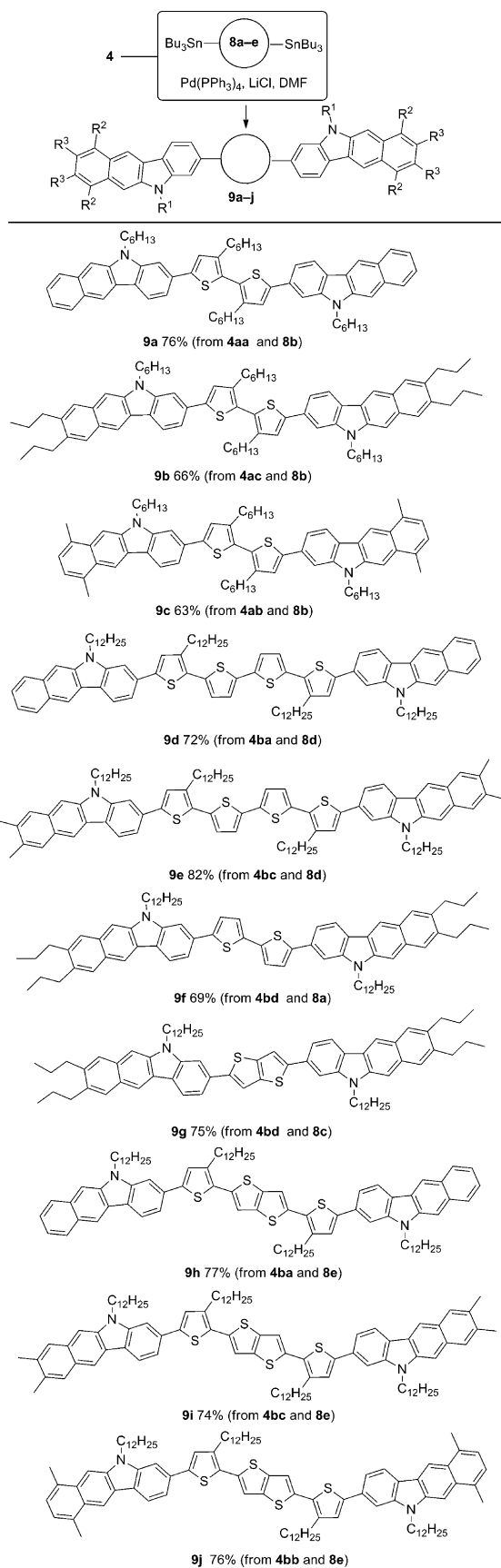


Figure 1. Synthesis of a library of end-capped oligothiophenes.

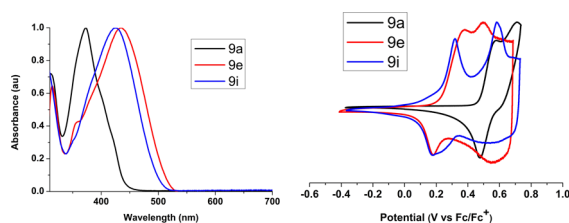


Figure 2. UV–vis spectra of **9a**, **9e**, and **9i** in CH_2Cl_2 solution (left) and cyclic voltammograms (right) as thin films on Pt electrodes.

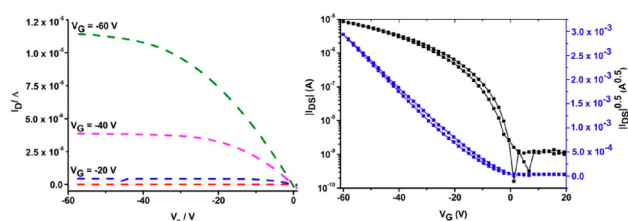


Figure 3. Transfer (right) and output (left) curves for **9e**.

suggests stability under ambient conditions and good charge injection from gold ($\Phi = 5.1$ eV). The addition of alkyl substituents on the outermost rings has the effect of raising the HOMO energy level, as does the incorporation of fused units in the central linkers.

Solution UV–vis spectra of compounds **9a**, **9e**, and **9i** are also shown in Figure 2. As expected, a red shift is observed upon extension of the central oligothiophene linker, while the addition of alkyl substituents has negligible impact on the appearance of the spectra. Optical band gaps were calculated from the absorption onset and LUMO energy levels and then were estimated using the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$. The optical and electrochemical properties of **9a–j** are collated in Table 1.

A preliminary investigation into the performance of compound **9e** in OFET devices has been carried out. Charge mobilities of $0.026 (\pm 0.003) \text{ cm}^2/(\text{V} \cdot \text{s})$ and $I_{\text{on}}/I_{\text{off}}$ ratios of 2×10^4 were obtained from top-contact devices

Table 1. Optical and Electrochemical Properties of **9a–9j**

	HOMO/ eV ^a	LUMO/ eV ^b	HOMO calcd ^c	LUMO calcd ^d	$\lambda_{\text{onset}}/$ nm ^e	$E_g/$ eV ^f
9a	−5.27	−2.46	−5.60	−1.29	442	2.81
9b	−5.16	−2.40	−5.46	−1.18	450	2.76
9c	−5.15	−2.39	−5.52	−1.25	450	2.76
9d	−5.22	−2.82	−5.37	−1.53	517	2.40
9e	−5.05	−2.66	−5.26	−1.91	518	2.39
9f	−5.30	−2.76	−5.48	−1.26	489	2.54
9g	−5.31	−2.64	−5.54	−1.14	465	2.67
9h	−5.24	−2.75	−5.42	−1.43	498	2.49
9i	−5.04	−2.56	−5.31	−1.43	499	2.48
9j	−5.09	−2.61	−5.34	−1.47	500	2.48

^a Calculated using the equation $E_{\text{HOMO}} (\text{eV}) = (-4.8 - E_{\text{onset}} + E_{1/2[\text{Fc}]})$.

^b Calculated using the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$. ^c See the Supporting Information for calculation of the negative of the ionization energies. ^d See the Supporting Information for calculation of the negative of the electron affinities. ^e Measured as dilute solutions in CH_2Cl_2 . ^f Calculated from the absorption onset measured by UV–vis spectroscopy.

fabricated by spin coating a 0.5% w/w solution in CHCl_3 onto a bare Si/SiO_2 (200 nm) wafer, followed by thermal annealing at 100 °C and evaporation of gold electrodes through a shadow mask. Transfer and output curves for **9e** are shown in Figure 3.

In summary, we have developed a new synthetic approach to benzo[*b*]carbazoles that utilizes key cyclization events triggered by the introduction and removal of a phase tag, in combination with tag-assisted purification methods. The approach has been used to generate a library of novel benzo[*b*]carbazole end-capped oligothiophene semiconductors for application in OFET devices. Work is currently underway to further investigate and optimize the properties and performance of these new materials.

Acknowledgment. We thank the EPSRC (S.C.C. and CASE award to M.T.L.) and SAFC Hitech (CASE award to M.T.L.) for financial support.

Supporting Information Available. Experimental details for the preparation of compounds and devices, ^1H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.