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Microwave synthesis and fluorous purification of 4-(tetrathienyl)butyric acid for self-assembled monolayer semiconductor applications

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Abstract

Microwave-promoted synthesis and fluorous purification procedures have been employed successfully to generate 4-(tetrathienyl)butyric acid rapidly. Initially, a fluorous tag 1*H*,1*H*-perfluorooctylamine was tethered to 4-(thienyl)butyric acid via an amide traceless linkage. Subsequent, sequential α-bromination and Stille cross-coupling reactions with 2-(tributylstannyl)thiophene grew the fluorous-tagged 4-(oligothienyl)butyric acid efficiently. Each synthetic transformation was followed by a fluorous-solid phase extraction procedure to isolate the fluorous-tagged compound intermediate in excellent yield. Finally, the fluorous tag was cleaved by microwave-promoted saponification of the amide bond to liberate the desired 4-(tetrathienyl)butyric acid.

Keywords: Self-assembled monolayer; Traceless fluorous tag; Organic semiconductor

Oligothiophenes are of significant interest for application as organic semiconductors in thin film transistor (TFT) devices.[1] The performance of these devices is dependent on the chemical structure of the organic semiconductor, the molecular assembly at the interface with the gate dielectric and the barrier to charge injection at the metal electrodes.[2] Commonly, the oligothiophene chemical structure is modified by varying the number of thiophene residues in conjugation and decorating the π-conjugated oligothiophene core with substituents.[3]

The performance of a TFT device may be improved significantly by controlling the molecular order within the oligothiophene semiconductor layer.[4] Oligothiophenes with appropriate chemical functionality will adsorb on the gate dielectric to form a stable supramolecular self-assembled monolayer (SAM). Previously, it had been shown that carboxylic acids adsorb on an aluminium oxide gate dielectric of a TFT,[5] which induces intermolecular π–π overlap between adjacent oligothiophenes and facilitates the transport of charge through the organic semiconductor layer by an intermolecular hopping mechanism.[6]

Generally, oligothiophenes are synthesised by palladium-catalysed cross-coupling reactions, which require heating for extended periods of time to force reaction equilibria towards completion.[7] These reaction times can be reduced significantly by employing microwave dielectric heating. The microwave electromagnetic radiation couples with the molecular dipoles of the solvent(s)/reagent(s); the oscillation of these molecules results in the homogeneous heating of the reaction mixture and rapid conversion of the starting material(s) to product(s).[8]

Oligothiophenes for organic electronics applications should be essentially free of impurities that affect the device performance and stability. Purification by chromatography, recrystallisation or sublimation is often laborious and provides oligothiophenes in low yield over extended time frames. Previously, we had reported a fluorous-solid phase extraction (F-SPE) strategy to facilitate the

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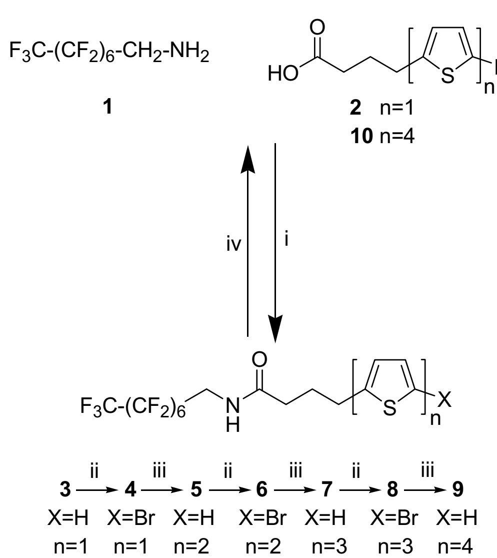
purification of organic semiconductors.[9] In this approach, a perfluorinated compound (>40% fluorine by molecular weight) was reacted with a stoichiometric amount of reagent(s).[10] Following each synthetic transformation, the crude product mixture (5–15% weight of fluorous-silica gel) was loaded onto a F-SPE cartridge and washed with a fluorophobic solvent to elute non-fluorinated material and then washed with a fluorophillic solvent to elute the pure fluorinated compound.[11]

Herein is reported a synthesis/purification strategy to generate 4-(oligothienyl)butyric acids for self-assembly on metal oxide surfaces. Initially, a traceless fluorous tag 1*H*,1*H*-perfluorooctylamine **1** was coupled to 4-(thienyl)-butyric acid **2** using a *N*′,*N*′-dicyclohexylcarbodimide (DCC)-mediated amide formation reaction to provide the corresponding fluorous-tagged compound **3** (100%).[12] Compound **3** was then reacted with *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) to give bromide **4** (71%).[13] A Stille cross-coupling reaction between bromide **4** and 2-(tributylstannyl)thiophene that was heated by microwave irradiation (1 min) furnished dimer **5** in good yield (76%).[14] The α-bromination and Stille cross-coupling reactions were repeated sequentially to afford **6** (72%), **7** (65%), **8** (77%) and **9** (65%). Finally, the traceless fluorous tag was cleaved by microwave-accelerated saponification of the amide bond to liberate **10** (80%) (Scheme 1).[15]

Intermediates **3**–**9** were isolated after each synthetic manipulation using a single F-SPE procedure. The crude product mixture was loaded onto a F-SPE column, and then washed with methanol/water (4:1) to elute non-fluorinated material. Subsequently, the F-SPE column was washed with tetrahydrofuran (THF) to elute the fluorous-tagged compound intermediate **3**–**9**. The final saponification reaction was followed by a facile extraction procedure to separate fluorous tag **1** from 4-(tetrathienyl)butyric acid **10**.



Scheme 1. Synthesis of compounds **3**–**10**. Reagents and conditions: (i) DCC, *N*,*N*-dimethylaminopyridine, CH_2Cl_2; (ii) NBS, DMF; (iii) 2-(tributylstannyl)thiophene, $Pd(PPh_3)_4$, ClC_6H_5, μW, 300 W, 190 °C, 150 mbar, 1 min, (iv) NaOH, ethyleneglycol, μW, 300 W, 180 °C, 150 mbar, 10 min.

The optical absorption ($\lambda_{max}^{ABS} = 398$ nm) and emission ($\lambda_{max}^{PL} = 458$ nm, 485 nm) spectra of **10** in CH_2Cl_2 solution were determined (Fig. 1).

The broad and unstructured absorption signal detected is a consequence of considerable rotation between individual thiophene residues that comprise **10**. Conversely, the emission signal has vibrational structure, which is consistent with the tetrathiophene core having increased planarity in the excited state. The large molar extinction coefficient ($\varepsilon = 9406$ mol^{-1} dm^3 cm^{-1}) indicates that these signals originate from the allowed π–π* transition associated with the tetrathiophene core. The optical band gap (E_g^{op}) was estimated from the intercept of the normalised absorption and emission spectra ($E_g^{op} = 3.12$ eV).

The electrochemistry of **10** was investigated by cyclic voltammetry to determine the energy of the highest occupied molecular orbital (HOMO).[16] The voltammogram showed a quasi-reversible one-electron first oxidation wave ($E_1^0 = 0.94$ V vs Fc/Fc$^+$), corresponding to the HOMO having an energy of −5.92 eV. The energy of the lowest unoccupied molecular orbital (−2.80 eV) was calculated by the addition of the optical band gap ($E_g^{op} = 3.12$ eV) to the energy value of the HOMO. In addition, an irreversible second oxidation wave ($E_2^0 = 1.17$ V vs Fc/Fc$^+$) and an irreversible reduction wave ($E_1^R = -1.16$ V vs Fc/Fc$^+$) were observed.

In conclusion, the high efficiency of this high-throughput methodology enabled the rapid generation of 4-(tetrathienyl)butyric acid **10**. Initially, a fluorous tag **1** was tethered to starting material **2** via a traceless amide linkage. Sequential α-bromination and microwave-accelerated Stille cross-coupling reactions in conjunction with F-SPE purification grew the oligothiophene rapidly. Finally, the traceless fluorous tag was cleaved by microwave-promoted saponification to liberate 4-(tetrathienyl)butyric acid **10** in excellent yield and purity. The optical absorption and emission spectra of **10** identified a high degree of rotational freedom between individual thiophene residues in the ground state and increased planarity in the excited state.

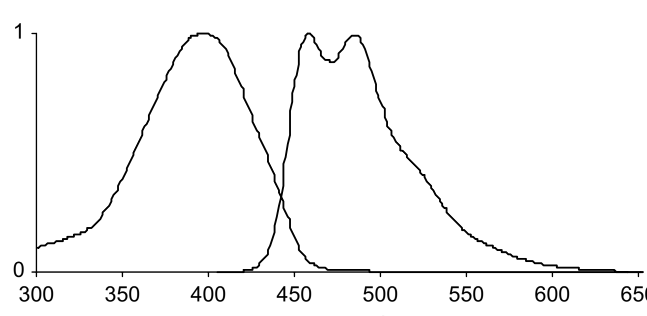


Fig. 1. Optical absorption and emission spectra of **10** in CH_2Cl_2. The emission spectrum was obtained by exciting a solution **10** in CH_2Cl_2 at 397 nm. Intensities are in arbitrary units.

We anticipate that this methodology could find generic application in the generation of novel functionalised π-conjugated materials for self-assembly on the gate dielectric of TFT devices.

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Supplementary data

Experimental procedures and spectroscopic data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.101.

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