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Synthesis of Novel Thiophene-Based Oligomers and Polymers with Thienothiadiazole Units

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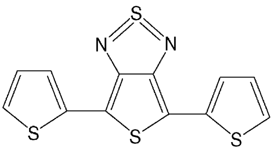
Summary: Novel non-alkylated and alkylated quinquethiophenes were prepared by the Stille coupling reaction of bis(5-bromo-2-thienyl)thieno[3,4-c][1,2, 5]thiadiazole (**TBr**) with 2-(tributylstannyl)thiophene. These compounds possess long wavelength absorption maxima around 700 nm in solution and 750 nm in thin films. Dibromo compound **TBr** is further employed as a building block in the syntheses of low-bandgap copolymers with fluorene units. A soluble alternating copolymer was prepared by the Suzuki coupling of **TBr** with bis(propane-1,3-diyl) 9,9-bis(2-ethylhexyl)fluorene-2,7-diylbisboro-nate. It shows the long-wavelength absorption maximum at 747 nm in solution and at 764 nm in thin film, which indicates extensively conjugated system.

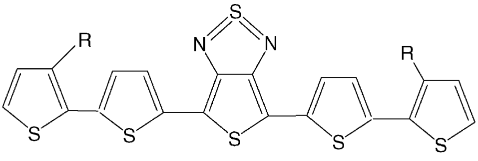
Keywords: 4,6-di(2-thienyl)thieno[3,4-c][1,2; 5]thiadiazole; oligothiophenes; thiophene-fluorene copolymer

Introduction

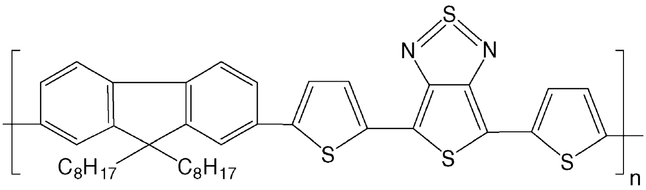
Polythiophenes and copolymers containing thiophene units are extensively studied because of their potential applications in optoelectronics, especially in organic photovoltaics.[1] 4,6-di(2-thienyl)thieno[3,4-*c*] [1,2, 5]thiadiazole, **T**, is highly planar terthiophene derivative first prepared by Tanaka et al.[2] Its central thienothiadiazole moiety has an electron-acceptor nature; its longest wavelength UV-vis absorption maximum lies at 620 nm. It is, therefore, interesting as a dopant for bulk heterojunction photovoltaic cells in blends with polythiophenes, but even more as a building block for the syntheses of low band-gap thiophene-based oligomers and donor-acceptor copolymers absorbing light in a great part of the solar spectrum. Here, we present our results on the syntheses of such compounds, with the structures shown below:



T



Q (R=H), **HexQ** (R = n-hexyl)



CTF

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Experimental Part

^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker Avance DPX-300 spectrometer at 300 MHz and 75 MHz, respectively, in $CDCl_3$ with hexamethyldisiloxane as internal standard. ^{13}C CP/MAS NMR spectra were measured on Bruker Avance 500 US/WB spectrometer (125 MHz, spinning speed 10 kHz, repetition delay 30 s, cross-polarization contact time 3 ms). FT IR spectra were measured on a Perkin-Elmer Paragon 1000 PC Fourier transform infrared spectrometer. The UV-Vis-NIR spectra were recorded on Perkin Elmer Lambda 35 spectrophotometer.

Results and Discussion

The starting terthiophene derivative **T** was prepared by five-step synthesis from thiophene, using some modifications of the described procedures.[3,4] Then, we concentrated on the syntheses of two classes of new compounds: (a) longer oligomeric analogues of terthiophene **T**; (b) alternating copolymers of **T** with dialkylfluorene comonomers (see above, **CTF**).

Synthesis of a key intermediate, 5,5′-dibromo derivative of **T**, denoted as **TBr**, was accomplished by a rapid bromination of **T** with a small excess of *N*-bromosuccinimide (NBS) in pyridine; the resulting mixture of mono-, di- and tribrominated derivatives was purified by column chromatography and repeated crystallization from toluene. The dark-blue compound **TBr,** obtained in 40% yield, has m.p. 206–209 °C and its solubility in common organic solvents is quite low; therefore its ^{13}C CP/MAS NMR spectra were measured in the solid state. The spectrum is displayed in Figure 1a along with numbering of atoms and tentative assignment of the observed peaks: $\delta = 110.1$ (C1), 120.7 (C6), 131.7 (C2, C4), 136.7 (C3), 155. (C5). The chemical structure was confirmed also by FT-IR spectroscopy and elemental analysis. $C_{12}H_4Br_2N_2S_4$: Calcd. C 31.05, H 0.87, N 6.03, S 27.62, Br 34.42; Found C 31.07, H 0.92, N 5.95, Br 35.08.

Non-alkylated quinquethiophene **Q** was prepared in 35% yield by the Stille coupling reaction of **TBr** with 2-(tributylstannyl)thiophene, according to the following general scheme (R = H):

This crystalline dark-green compound, melting at 179–181 °C, was sparingly soluble in common solvents, therefore its ^{13}C CP/MAS NMR spectra were measured in solid state: $\delta = 120.2$ (C10), 122.5–124.4 (C1, C3, C6, C7), 128.2 (C2), 133.3–138.6 (C4, C5, C8), 154.3–157.4 (C9). The chemical structure was further confirmed by FT-IR spectra and elemental analysis. $C_{20}H_{10}N_2S_6$: Calcd. C 51.04, H 2.14, N 5.95, S 40.87; Found C 51.70, H 2.94, N 5.14.

Since alkyl derivatives of **Q** should have better properties (e.g., better solubility and film formation), and could also serve as more suitable intermediates for the build-up of longer soluble oligomers and copolymers, we focused our further attention to the syntheses of such materials. In this work we deal with the synthesis of the alkylated analogue **HexQ** (R = hexyl).

The starting compound **TBr** rapidly decolorizes (its thiadiazole bridge is probably destroyed) in the presence of Grignard reagents, and, consequently, the synthesis of **HexQ** by Grignard metathesis of **TBr** with excess of Grignard reagent prepared from 3-alkyl-2-bromothiophene is not feasible. Therefore, we prepared 2-(tributylstannyl)-3-hexylthiophene, which reacted with **TBr** by the Stille coupling (see Scheme 1, R = hexyl). After purification of the reaction product by repeated column chromatography, quinquethiophene derivative **HexQ** was obtained in 24% yield as viscous dark-green oil.

^{13}C NMR spectra: $\delta = 14.2$ (C17), 22.72 (C16), 29.5–32.0 (C15-C12), 124.0 (C6), 124.8 (C7), 126.7 (C1), 130.3 (C2), 134.6 (C5, C8), 136.4 (C3), 140.1 (C4), 156.4 (C9). ^{1}H NMR spectra: $\delta = 0.90$ (d, H10), 1.31–1.39 (m, H7-H9), 1.63 (m, C6), 2.79 (m, C5), 6.92 (d, C2), 7.06 (d, C1), 7.16 (s, C3), 7.48 (m, C4).

$C_{32}H_{34}N_2S_6$: Calcd. C 60.14, H 5.36, N 4.38, S 30.11; Found C 60.53, H 5.50, N 4.25.

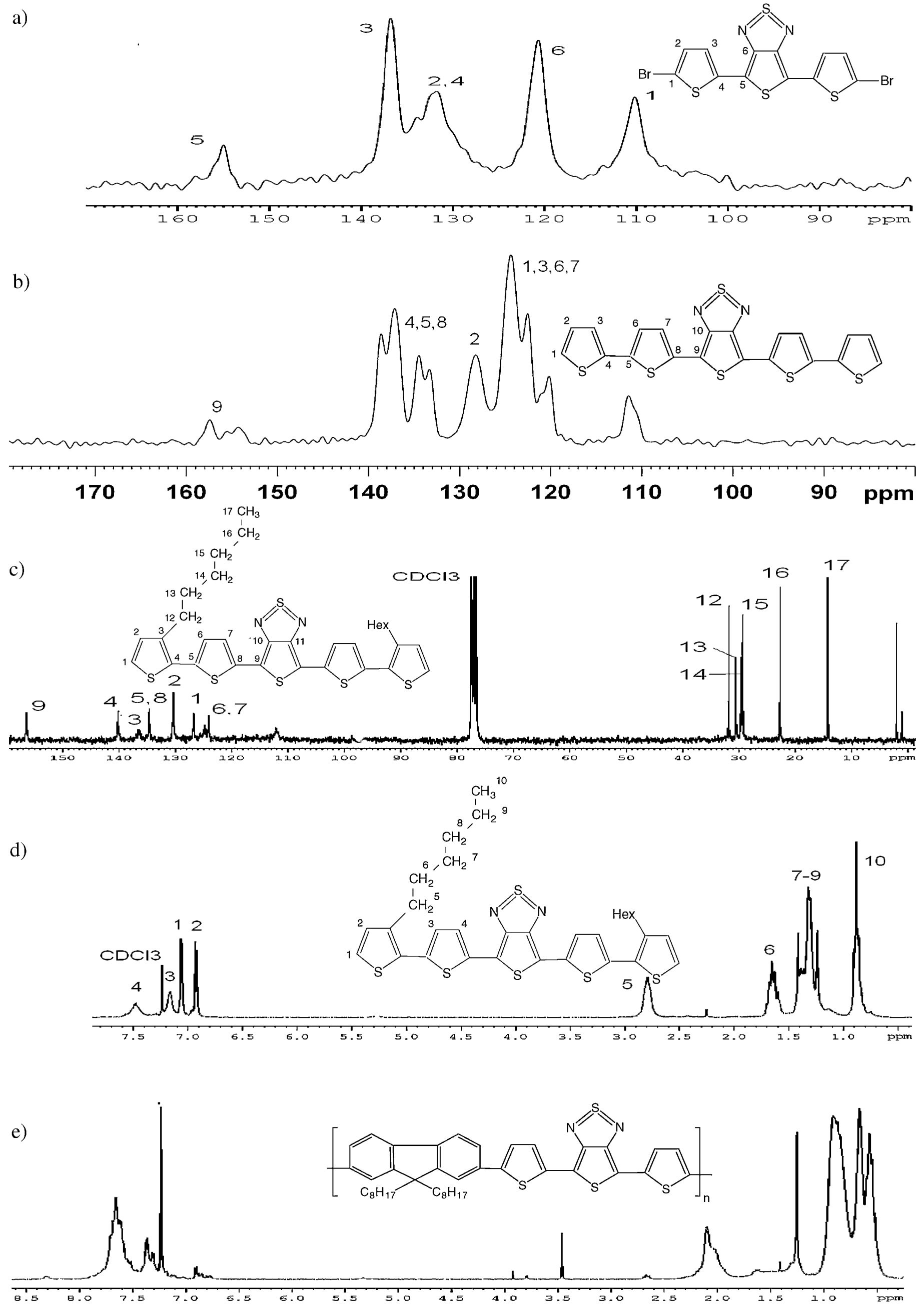
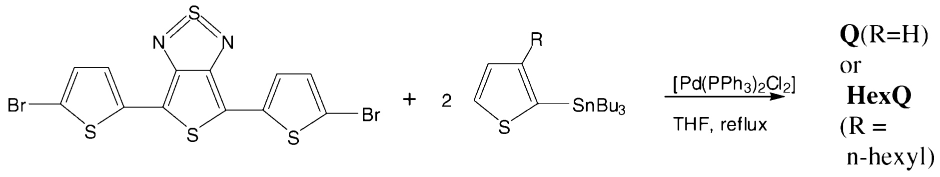


Figure 1.

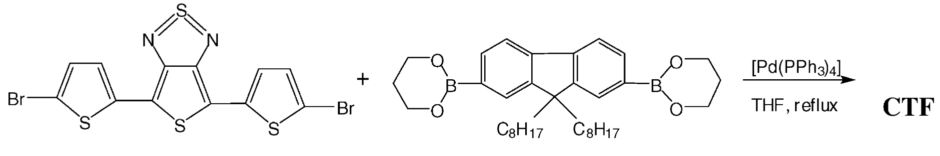
(a), (b): ^{13}C CP/MAS NMR spectra of **TBr** and **Q** in the solid state; **(c)** ^{13}C NMR spectra of **HexQ** in CDCl$_3$, **(d)** ^{1}H NMR spectra of **HexQ** in CDCl$_3$; **(e)** ^{1}H NMR spectra of **CTF** in CDCl$_3$.

Its chemical structure was confirmed also by FT-IR spectra.

Alternating copolymer **CTF** was synthesized by the Suzuki coupling reaction of **TBr** with commercially available bis(propane-1,3-diyl) 9,9-bis(2-ethylhexyl)fluorene-2,7-bisboronate (Sigma-Aldrich), according to the following scheme:



Scheme 1.



Scheme 2.

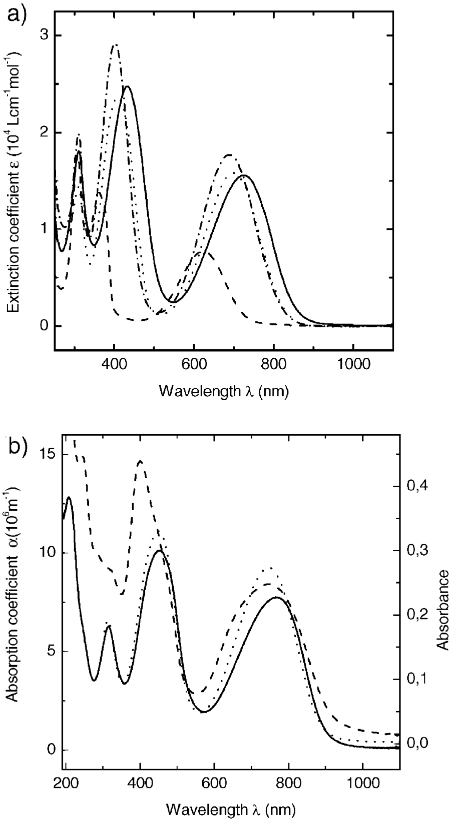


Figure 2.

UV-vis absorption spectra of prepared compounds; (a) in $CHCl_3$ solutions: **T** (dashed), **Q** (dotted), **HexQ** (dash and dot), **CTF-L** (solid); (b) in thin films on fused silica: **Q** (dashed), **CTF-H** (solid); the spectrum of **CTF-H** (dotted) in 1,2-dichlorobenzene solution is added for comparison.

After 20-h reaction, the polymer was end-capped first with fluorene comonomer and then with bromobenzene. One third of the resulting dark-green copolymer was soluble in THF, $CHCl_3$ or toluene and the rest was partially soluble in chlorobenzene. The lower (better soluble) fraction **CTF-L** has M_w 5400, $M_w/M_n = 2{,}4$ (according to GPC in THF). In the ^1H NMR high-resolution spectrum of the **CTF-L** ($CDCl_3$ at 330 K), the signals at 7.25–7.4 ppm can be assigned to the protons on the thiophene rings and their broadening can be explained by the relative rigidity of the conjugated polymeric structure. The signals of aromatic protons of the fluorene unit were detected as a broad peak at 7.66 ppm. The signals of the attached 2-ethylhexyl groups are at 2.10 (CH_2 next to fluorene unit), 0.91 (other CH_2), 0.67 and 0.57 (both end CH_3) ppm.

$C_{41}H_{44}N_2S_4$: Calcd. (for endless alternating copolymer) C 71.05, H 6.40, N 4.04, S 18.50; Found C 69.97, H 6.42, N 3.54.

The UV-vis absorption spectra of the prepared compounds measured in $CHCl_3$ solutions are shown in Figure 2a. In all spectra, three maxima are present. Absorption maxima of the trimer **T** are located at 308, 362 and 620 nm. For **Q** and **HexQ,** the shortest-wavelength maximum is located at 310 nm, nearly at the same position as for **T**, whereas the other two maxima are significantly red-shifted (407 and 699 nm in **Q**;

402 and 689 nm in **HexQ)**. Copolymer **CTF** in solution possesses the shortest-wavelength maximum at 310 nm, i.e. at the same position as in **Q** and **HexQ,** whereas the other maxima were even more red-shifted than in the case of **Q** and **HexQ** (432 and 725 nm in **CTF-L**; 451 and 747 nm in **CTF-H**). The UV-vis absorption spectra of thin films are shown in Figure 2b, where the absorption spectrum of **CTF-H** in 1,2-dichlorobenzene solution is also displayed for comparison. Absorption maxima of thin film of **Q** were located at 400 and 750 nm. It is apparent that the long-wavelength maximum is significantly red-shifted, when compared with the spectrum in solution, which indicates strong intermolecular interactions in the solid phase. Absorption spectrum of **CTF-H** as thin film exhibited maxima at 316, 451 and 766 nm. Compared with the spectrum in solution, the red shift of the long-wavelength maximum was also observed, but not so large as for **Q**.

It can be concluded that the attaching of two thiophene rings to terthiophene derivative **T** considerably increases the conjugation length, particularly in the case of more planar non-alkylated quinquethiophene **Q**. Compound **CTF** is a highly conjugated copolymer with alternating electron-donor and electron-acceptor units and, therefore, is quite interesting as a material for subsequent photophysical studies, especially in the field of photovoltaics.

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