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Received May 21, 2001

Activated dihydridocarbonyltris(triphenylphosphine)ruthenium catalyzes the cyclodimerization of both bis(2-thienyl)acetylene and bis(3-thienyl)acetylene to yield, respectively, 4,5,6-tris(2'-thienyl)benzo[*b*]thiophene and 5,6,7-tris(3'-thienyl)benzo[*b*]thiophene. These fluoresce in the blue. Both undergo irreversible one electron oxidation at ~1.1 mV versus Ag/Ag⁺ electrode, consistent with oxidation of the benzo[*b*]thiophene nuclei rather than the substituent thiophene rings.

J. Heterocyclic Chem., **39**, 91 (2002).

Results and Discussion.

Benzo[*b*]thiophenes are important heterocycles. These have often been prepared by construction of the thiophene ring by cyclization of suitable benzene derivatives [1-5]. Less often benzo[*b*]thiophenes have been prepared by annulation of the benzene ring onto a suitable thiophene nucleus [6-8].

While there is considerable interest in the application of transition metal catalysis to organic synthesis [9], benzo[*b*]thiophenes have not been previously prepared by transition metal catalyzed reactions. We recently reported the cyclodimerization of diphenylacetylene to yield 1,2,3-triphenylnaphthalene catalyzed by dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru) which has been activated by treatment with a stoichiometric amount of styrene [10]. This process yields ethylbenzene and a coordinately unsaturated active Ru complex. A Rh complex was used in a related example to catalyze the cyclodimerization of acetylenes to give naphthalenes [11]. These unique examples of acetylene cyclodimerization stand in contrast to the well-known transition metal catalyzed cyclotrimerization of acetylenes to yield benzene derivatives.

Herein, we report the preparation and properties of 4,5,6-tris(2'-thienyl)benzo[*b*]thiophene (I) and 5,6,7-tris(3'-thienyl)benzo[*b*]thiophene (II) by the activated Ru

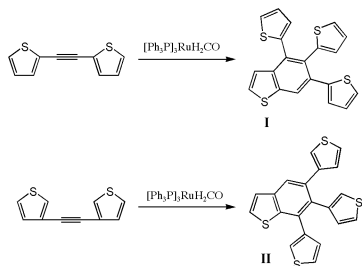


Figure 1 Ru catalyzed cyclodimerization of bis(thienyl)acetylenes.

catalyzed cyclodimerization of bis(2-thienyl)acetylene and bis(3-thienyl)acetylene, respectively. In both reactions, small amounts of the corresponding hexakis(2-thienyl)benzene and hexakis(3-thienyl)benzene formed by cyclotrimerization were found [12].

These novel compounds have been characterized by ¹H, ¹³C NMR, IR, UV-vis and fluorescence spectroscopy. Of note, they fluoresce in the blue (Figure 2). There is considerable interest in such materials [12].

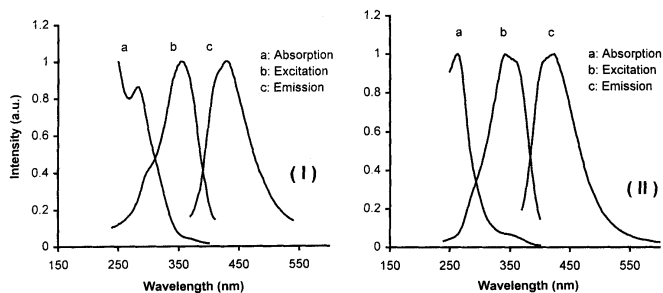


Figure 2 Absorption, emission and excitation spectra of I and II.

Their electrochemistry has also been examined. Both I and II undergo irreversible oxidation at 1.10 V versus a standard Ag/AgCl electrode. While benzo[*b*]thiophene undergoes one electron oxidation at 1.10 V versus a Ag/AgCl electrode [13]. Monosubstituted thiophenes undergo oxidation around 1.40 V. [14]. On this basis, we believe that both I and II undergo irreversible oxidation of their benzo-thiophene nuclei rather than oxidation of their pendant thiophene substituents.

EXPERIMENTAL

Five percent w/v CDCl₃ solutions were used to acquire ¹H, ¹³C NMR spectra on a Bruker AMX-500 MHz spectrometer. ¹³C NMR spectra were obtained with broadband proton decoupling.

All spectra were referenced to internal TMS. IR spectra of neat liquid films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Low resolution mass spectra were obtained on a Hewlett-Packard 5890 series II GC equipped with a Hewlett-Packard 5971 mass selective detector and a 30 meter DB-5 capillary column. Exact masses were determined by high resolution mass spectroscopy at the University of California Riverside Mass Spectroscopy center on a VG-ZAB instrument. Elemental analysis data was obtained at the Analytical Laboratories of Zhejiang University. A Princeton Applied Research (EG&G) electrochemistry system connected to a Potentiostat Galvanostat Model 283 was used to record the cyclic voltammetry. The working electrode is glassy carbon, while the reference electrode is standard Ag/AgCl electrode.

Ru catalyst (55 mg, 0.060 mmol) [15], 6 mL toluene and 6.8 μ L styrene were placed in a pressure tube which was purged with argon for 15 minutes. The tube was heated at 100 °C until the color of the solution turned into red-brown. Then, bis(2-thienyl)acetylene (0.38 g, 2 mmol) [16] was added, purged with argon for another ten minutes, kept at 135 °C for 24 hours. It was then cooled to room temperature. The mixture was concentrated and separated by the column chromatography (eluant: hexanes:dichloromethane = 8:2). In this way, 0.24 g (63%) of 4,5,6-tris(2'-thienyl)benzothiophene and 0.02 g (5%) hexakis(2-thienyl)benzene was isolated.

4,5,6-tris(2'-Thienyl)benzothiophene.

This compound has mp 145-146 °C; ¹H NMR: δ 8.08 (s, 1H), 7.43 (d, 1H, $J = 5.5$ Hz), 7.28 (dd, 1H, $J = 4.5$ and 1.5 Hz), 7.25 (d, 1H, $J = 5.5$ Hz), 7.21 (dd, 1H, $J = 5.0$ and 1.5 Hz), 7.19 (dd, 1H, $J = 5.0$ and 1.5 Hz), 6.96 (m, 2H), 6.89 (dd, 1H, $J = 5.0$ and 3.5 Hz), 6.85 (dd, 1H, $J = 4.5$ and 1.0 Hz), 6.82 (dd, 5.5, 1H, $J = 5.5$ and 4.0 Hz), 6.71 (dd, 1H, $J = 3.5$ and 1.0 Hz); ¹³C NMR: δ 143.2, 140.2, 140.0, 139.9, 139.7, 132.3, 131.5, 130.0, 129.8, 128.4, 127.5, 127.0, 126.6, 126.5, 126.3, 126.2, 126.1, 124.4, 123.9, 123.8; IR: ν 3100, 3077, 2925, 2854, 1623, 1411, 1387, 1244, 1233, 1088, 1080, 852, 836, 829, 815, 795, 748, 730, 709, 699, 693, 668 cm^{-1} ; HRMS Found: m/z : 379.9813. Calcd for C₂₀H₁₂S₄ 379.9822. Anal. Calc. for C₂₀H₁₂S₄: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.06; H, 3.18; S, 33.80.

hexakis(2-Thienyl)benzene [12].

This compound has ¹H NMR: δ 7.09 (d, 1H, $J = 5.0$ Hz), 6.68 (dd, 1H, $J = 5.0$ and 3.0 Hz), 6.59 (d, 1H, $J = 3.0$ Hz); ¹³C NMR: δ 140.7, 137.1, 129.1, 126.2, 125.8.

In a similar manner, bis(3-thienyl)acetylene (0.38g, 2 mmol) [16] was reacted as above. After chromatography, 5,6,7-tris(3'-thienyl)benzo[b]thiophene 0.22 g (58%) and hexakis(3-thienyl)benzene 0.015 g (4%) were obtained.

5,6,7-tris(3'-Thienyl)benzo[b]thiophene.

This compound has mp 121-122 °C; ¹H NMR: δ 7.91 (s, 1H), 7.47 (d, 1H, $J = 5.5$ Hz), 7.40 (d, 1H, $J = 5.5$ Hz), 7.31 (dd, 1H,

$J = 3.0$ and 1.5 Hz), 7.20 (dd, 1H, $J = 5.0$ and 3.0 Hz), 7.12 (dd, 1H, $J = 5.0$ and 3.0 Hz), 7.04 (dd, 1H, $J = 5.0$ and 3.0 Hz), 7.02 (dd, 1H, $J = 3.5$ and 1.5 Hz), 6.83 (dd, 1H, $J = 5.0$ and 1.0 Hz), 6.74 (dd, 1H, $J = 5.0$ and 1.0 Hz), 6.71 (dd, 1H, $J = 2.5$ and 1.0 Hz), 6.60 (dd, 1H, $J = 4.5$ and 1.5 Hz); ¹³C NMR: δ 142.5, 140.8, 140.0, 139.7, 138.9, 134.1, 131.4, 130.7, 130.2, 129.1, 128.8, 128.0, 124.8, 124.7, 124.4, 124.2, 124.1, 123.9, 123.7, 122.7; IR: ν 3102, 2925, 2855, 1624, 1437, 1412, 1347, 1321, 1265, 1177, 1100, 1080, 864, 836, 791, 749, 709, 677, 667, 658 cm^{-1} ; HRMS Found: m/z : 379.9831. Calcd for C₂₀H₁₂S₄ 379.9822.

Anal. Calc. for C₂₀H₁₂S₄: C, 63.18; H, 3.18; S, 33.70. Found: C, 63.06; H, 3.18; S, 33.75.

hexakis(3-Thienyl)benzene.

This compound has ¹H NMR: δ 6.92 (dd, 1H, $J = 4.5$ and 3.5 Hz), 6.59 (dd, 1H, $J = 3.5$ and 1.5 Hz), 6.50 (dd, $J = 4.5$ and 1.5 Hz) ppm; ¹³C NMR: δ 140.3, 136.5, 129.8, 124.1, 123.3 ppm; HRMS Found: m/z : 569.9712. Calcd for C₂₀H₁₂S₄ 569.9733.

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