

Supplementary electronic information

Electrosynthesis and characterization of verdazyl radical functionalized oligo/polythiophenes

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Table of content

- I. Generalities
- II. Synthesis of 2, 4-diisopropyl-6-terthiophene-3-oxotetrazane (2)
- III. Synthesis of 1,5-diisopropyl-3-terthiophene-6-oxoverdazyl (3)
- IV. ESR spectra of 1,5-diisopropyl-3-terthiophene-6-oxoverdazyl (3)
- V. Electrochemistry of (2)

I. Generalities

All reactions and manipulations were carried out under an argon atmosphere. Solvents were dried over activated molecular sieves (4 Å), and distilled under an atmosphere of argon prior to use. All reagents were purchased from Sigma-Aldrich and used as received. ¹H proton (¹³C carbon) NMR spectra were recorded on a 500 MHz (125 MHz) Bruker spectrometer. The NMR samples were prepared by dissolving 20 mg of product in 1 mL of deuterated solvent (DMSO-d₆ or CDCl₃). IR spectra were recorded as KBr pellet using a Bruker Fourier-transform infrared spectrophotometer. EPR spectra were recorded using a Varian E109 EPR Spectrometer. The EPR samples were subjected to a number of freeze-thaw cycles on a vacuum line prior to analysis. The EPR spectra were simulated using the WINSIM program. HRMS experiments were recorded on an Agilent 1260 Infinity liquid chromatograph/6530 accurate mass Q-TOF in high resolution mode in 70:30 acetonitrile/water using positive mode electrospray ionization (HPLC grade solvents).

II. Synthesis of 2, 4-Diisopropyl-6-terthiophene-3-oxotetrazane (2)

0.50 g (1.8 mmol) of 2, 4-diisopropylcarbonohydrazide bis-hydrochloride (**1**) and 0.38 g (1.8 mmol) of 2,2':5',2''-terthiophene-3'-carboxaldehyde were dissolved in 10 mL of dry ethanol. To this mixture was added 0.30 g (3.8 mmol) of sodium acetate in ethanol and stirred at room temperature. The reaction was followed by TLC. After 24 hours, the mixture was filtered and evaporated to obtain the crude product. The purification of the residue by a silica gel column chromatography with 40 % ethyl ether and 60 % CH₂Cl₂ as eluent gave the tetrazane (**2**) (R_F = 0.43) as a yellow solid (0.31 g, 0.71 mmol). Yield: 40 %; ¹H NMR (DMSO-d₆, 500 MHz); δ(ppm) = 0.95 (d, *J* = 6.4 Hz, 6H, -C(CH₃)₂), 1.01 (d, *J* = 6.7 Hz, 6H, -C(CH₃)₂), 4.45 (m, 2H, CH(CH₃)₂), 4.56 (t, *J* = 11.5 Hz, 1H, CH-N), 5.25 (d, *J* = 11.5 Hz, 2H, NH), 7.12 (t, *J* = 3.7 Hz, 1H, Th-H), 7.18 (t, *J* = 3.7 Hz, 1H, Th-H), 7.29-7.35 (m, 2H, Th-H), 7.56 (d, *J* = 4.7 Hz, 1H, Th-H), 7.60 (s, 1H, Th-H), 7.69 (d, *J* = 4.9 Hz, 1H, Th-H). ¹³C NMR (DMSO-d₆, 125 MHz); δ(ppm) = 18.7, 19.5, 46.7, 67.5, 124.0, 124.6, 126.2, 127.6, 128.0, 128.2, 128.5, 131.9, 133.0, 134.2, 135.5, 135.6, 153.0. IR (KBr pellet); ν(cm⁻¹) = 1607 (CO). HRMS (ESI) for C₂₀H₂₄N₄OS₃ [M+H]⁺: calcd. 433.1190; found 433.1186.

III. Synthesis of 1,5-diisopropyl-3-terthiophene-6-oxoverdazyl (**3**)

0.10 g (0.23 mmol) of 2, 4-diisopropyl-6'-terthiophene-3-oxotetrazane (**2**) and 0.037 g (0.34 mmol) of 1,4-benzoquinone were refluxed in 5 mL of toluene. The reaction was followed by TLC. After 3 hours, the mixture was cooled, filtered and the solvent removed by evaporation to get the crude product. Pure **3**, a red oil, was obtained by eluting the residue through a silica gel column using 100 % CH₂Cl₂ (R_F = 0.43) as the eluent. The red oil crystallized upon sitting for few days. Yield: 70 %; IR (KBr pellet); $\nu(\text{cm}^{-1}) = 1680$ (CO ketone). HRMS (ESI) for C₂₀H₂₁N₄OS₃ [M⁺]: calcd. 429.0877; found 429.0870.

IV. ESR spectra of 1,5-diisopropyl-3-terthiophene-6-oxoverdazyl (**3**)

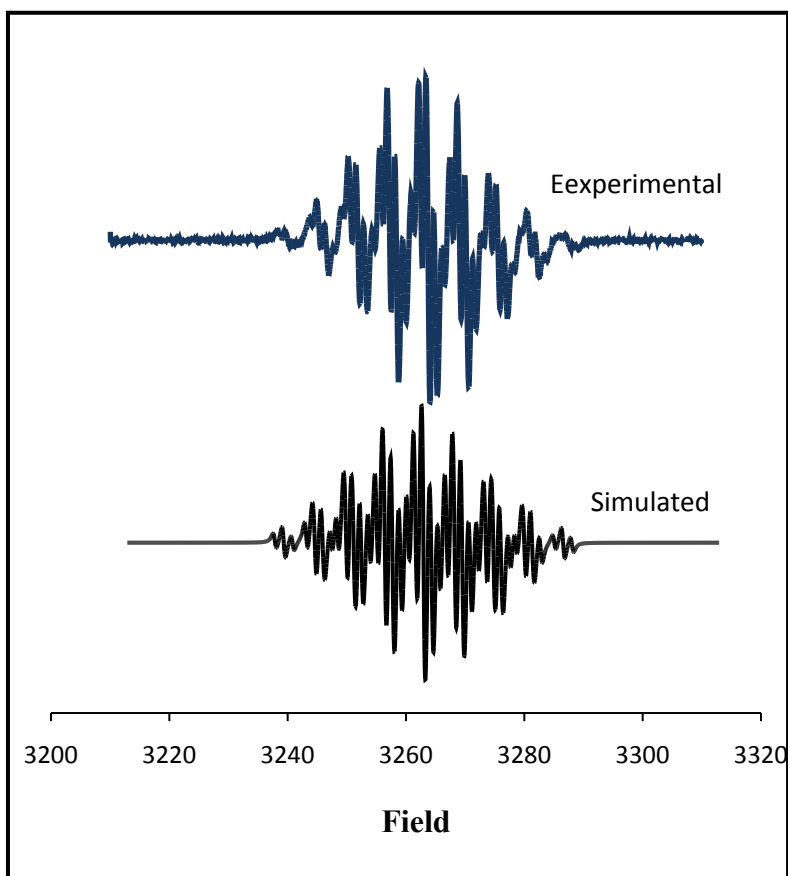


Figure 1S. Experimental EPR spectrum of radical **3** recorded at room temperature (top) and simulated spectrum (bottom)

V. Electrochemistry of (2)

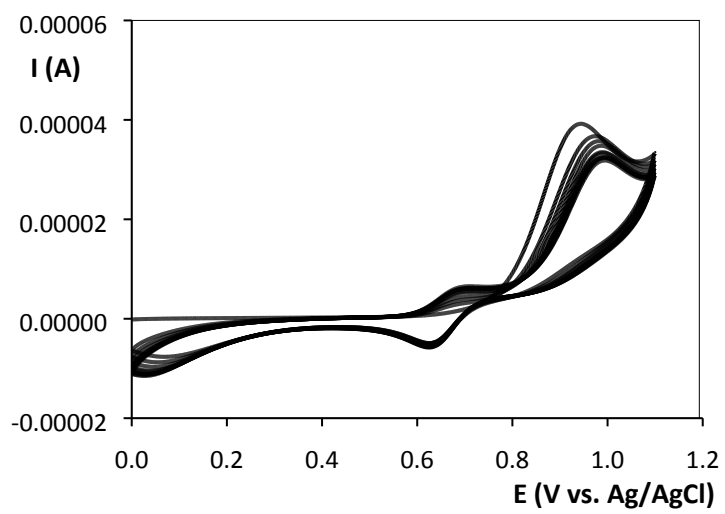


Figure 2S. Repeated CV scans of **2** at 1.1 V. Scan rate: 0.1 V/s. WE: Pt, CE: Pt wire, RE: Ag/AgCl.