

Electronic Supplementary Information

Electron reduction processes of nitrothiophenes. A systematic approach by DFT Computations, Cyclic Voltammetry and E-ESR Spectroscopy

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Synthetic details. The ^1H NMR spectra were recorded at 300 or 400 or 600 MHz with a Varian Gemini 300 or a Varian Mercury-Plus 400 or a Varian Unity-INOVA 600 spectrometer, respectively. ^1H Chemical shifts are reported in ppm from tetrametilsylane and referred to the solvent resonance (CDCl_3 : 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Unity-INOVA 600 spectrometer and chemical shifts are referenced to the solvent (CDCl_3 : 77.0 ppm). ESI mass spectra (m/z) were recorded on a Waters – Micromass ZQ4000. Melting points were measured with a Büchi 535 apparatus and are uncorrected. Flash chromatography (fc) was performed on silica gel (0.040–0.063 mm). Thin-layer chromatography (tlc) was carried out using precoated silica gel on PET foils (Fluka) with fluorescent indicator 254 nm and spots were revealed by an UV lamp. All the products were synthesized according with the quoted literature procedure, however, where the experimental procedure differed significantly from that published or when some spectral data of the products have not been previously reported, related details have been included. 2-Nitrothiophene (**1**) was purchased from Fluka and recrystallized from light petroleum; it contains an impurity of 3-nitrothiophene (13%, determined by ^1H -NMR spectroscopy). 3-Nitrothiophene^{1,2} (**2**) was prepared according to literature method.³ 2,5-Dinitrothiophene^{4,5} (**3**) and 2,4-dinitrothiophene^{6,7} (**4**) were obtained as mixture (**4** being the major product) according to literature⁸ and separated by column chromatography (dichloromethane/hexane: 6/4). 3,4-Dinitrothiophene (**5**) was obtained slightly modifying the synthetic procedure reported in the literature⁹ that required firstly the displacement of one bromine atom from 2,5-dibromo-3,4-dinitrothiophene through treatment with hypophosphorous acid in acetone then the removal of the second bromine atom with copper in boiling butanoic acid. In the modified procedure the two bromine atoms can be removed from the dibrominated precursor in a single step using copper in acetic acid at 75 °C, as follows. Copper powder (10 g, 0.16 mol) was added stepwise (in a time of 1 h) to a solution, heated at 75 °C and magnetically stirred, of 2,5-dibromo-3,4-dinitrothiophene (8.5 g, 0.025 mol) in 50 mL of acetic acid. The reaction mixture was kept at 75 °C for further 2 h then allowed to stand until room temperature. The mixture was poured into cold water and filtered on a Buchner funnel. The solid obtained, containing compound **5** mixed to unreacted copper powder, was transferred into a becker, treated with dichloromethane and decanted in order to extract the organic matter from the mixture. This extraction was repeated until to the complete removal of organic compounds from the crude solid, monitored by tlc analysis (light petroleum/diethyl ether: 7/3). The combined organic layers were dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure and the residue was purified by fc over silica gel

(light petroleum/diethyl ether: 7/3). 3.27 g (75% yield) of 3,4-dinitrothiophene^{9,10} (**5**) were obtained as pale yellow solid: ¹³C NMR (151 MHz, CDCl₃, 25°C): δ 128.03, 141.3. 2,3,4-Trinitrothiophene⁹ (**6**) was obtained by following the literature procedure.⁹ After purification by column chromatography on silica gel (dichloromethane/hexane: 6/4) compound **6** was obtained in 73% yield as white solid, m.p.: 140-142 °C (Lit.⁹ 138-141 °C), ¹H NMR (600 MHz, CDCl₃): δ 8.57 (1H, 1s); ESI-MS (-): (m/z) = 218 (M-H)⁻. 2-Nitrobenzo[*b*]thiophene^{11,12,13} (**7**) and 3-nitro[*b*]thiophene^{11,14} (**8**) were synthesized and purified according to literature procedures.¹⁵ NMR data reported in ref. 21 are in DMSO-d₆ and in CD₃OD, herein we report NMR data in CDCl₃. 2-Nitrobenzo[*b*]thiophene (**7**): ¹H NMR (400 MHz, CDCl₃): δ 7.49 (1H, ddd; *J* = 8.2, 7.2, 1.1 Hz), 7.58 (1H, ddd; *J* = 8.2, 7.2, 1.3 Hz), 7.84 (1H, ddd; *J* = 8.2, 1.7, 0.7 Hz), 7.94 (1H, dddd; *J* = 8.2, 1.7, 0.7, 0.3 Hz), 8.22 (1H, d; *J* = 0.7 Hz). 3-nitrobenzo[*b*]thiophene (**8**): ¹H NMR (400 MHz, CDCl₃): 7.52 (1H, dddd; *J* = 8.3, 7.1, 1.3, 0.4 Hz), 7.61 (1H, ddd; *J* = 8.3, 7.1, 1.1 Hz), 7.89 (1H, dddd; *J* = 8.3, 1.1, 0.8, 0.4 Hz), 8.62 (1H, dddd; *J* = 8.3, 1.3, 0.8, 0.4 Hz), 8.7 (1H, d; *J* = 0.4 Hz). 2-Nitrobenzo[*b*]furane^{13,16} (**9**) was synthesized and purified according to the literature procedure.^{17,18}

Electrochemical Details. The redox behaviour of the investigated compounds was studied by cyclic voltammetry (CV); all electrochemical measurements were performed under nitrogen atmosphere, at room temperature, using a single compartment, three electrode cell in acetonitrile (freshly distilled over P₂O₅) solution with 0.1 M (n-Bu)₄ NPF₆ as supporting electrolyte, containing the studied compound at *ca.* 2 mM concentration.

The CVs were recorded using an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat controlled by a personal computer *via* GPES software. The working electrode was a glassy carbon disk, 5 mm diameter, sealed inside a Teflon support and the counter electrode was a Pt wire. After a preliminary checking that the voltammograms were not water sensitive, which was carried out with a silver wire used as pseudo-reference electrode, all the electrochemical measurements were repeated with an aqueous saturated calomel electrode (SCE).

The reduction potential values reported in the paper are referred to the ferrocinium/ferrocene (Fc⁺/Fc) couple, as recommended by IUPAC.¹⁹ The formal potential of this redox couple, determined from voltammetric studies, was 0.363 V vs SCE. Generally, the CVs were recorded at different potential scan rates, from 50 to 500 mV/s. For each scan rate four voltammograms were sequentially recorded. For all the nitrothiophenes the value of the

cathodic peak (E_{pc}), recorded at the scan rate of 50 mV/s is always reported; when a redox couple displays a reversible or a quasi-reversible behaviour the value of the formal potential (E°) is also calculated from the half-sum of the cathodic and anodic peak potentials.

E-EPR Details. EPR spectra were recorded at room temperature using an ELEXYS E500 spectrometer equipped with a NMR gaussmeter for the calibration of the magnetic field and a frequency counter for the determination of g -factors that were corrected against that of the perylene radical cation in concentrated sulfuric acid ($g = 2.002583$). The electrochemical cell was home-made and consisted of an EPR flat cell (Wilma WG-810) equipped with a $25 \times 5 \times 0.2$ mm platinum gauze (cathode), a platinum wire (anode). The current was supplied and controlled by an AMEL 2051 general-purpose potentiostat.

In a typical experiment, the cell was filled with a acetonitrile solution of the appropriate substrate (*ca.* 1 mM) containing tetrabutylammonium perchlorate (*ca.* 0.1 M) as supporting electrolyte. After thoroughly purging the solution with N_2 , spectra were recorded at different potential settings in the range 0 to -5.0 V.

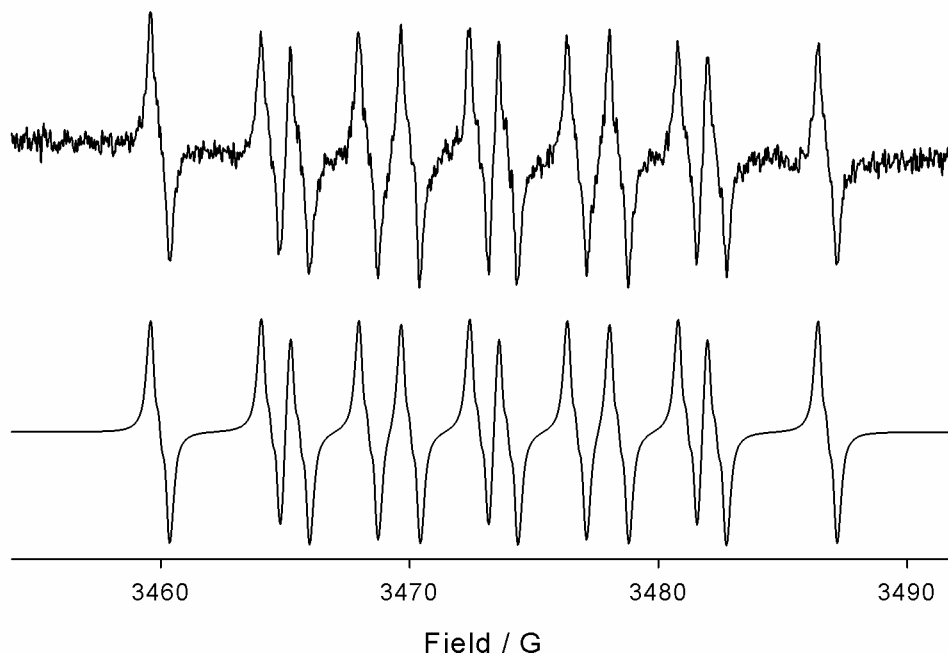


Figure S1. ESR spectrum (top) of the radical species electrogenerated from **4** (1 mM) in 0.1 M Bu_4NClO_4/CH_3CN at $E_{app1} = E_1^0$ and the corresponding theoretical simulation (bottom) obtained with the spectroscopic parameters reported in Table 1 in the manuscript.

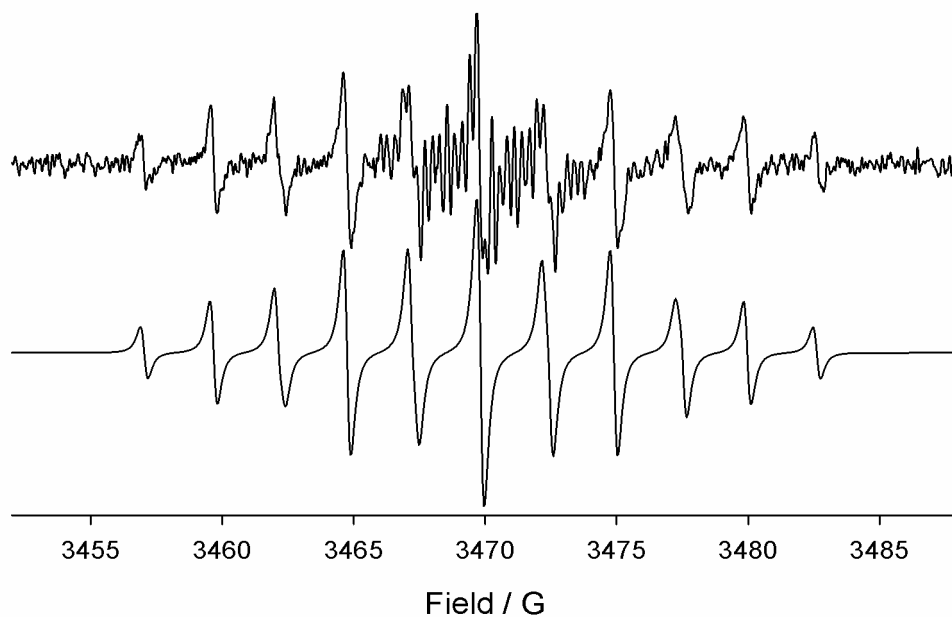


Figure S2. ESR spectrum (top) of the radical species electrogenerated from **5** (1 mM) in 0.1 M Bu₄NClO₄/CH₃CN at $E_{\text{appl}} = E_1^0$ and the corresponding theoretical simulation (bottom) obtained with the spectroscopic parameters reported in Table 1 in the manuscript.

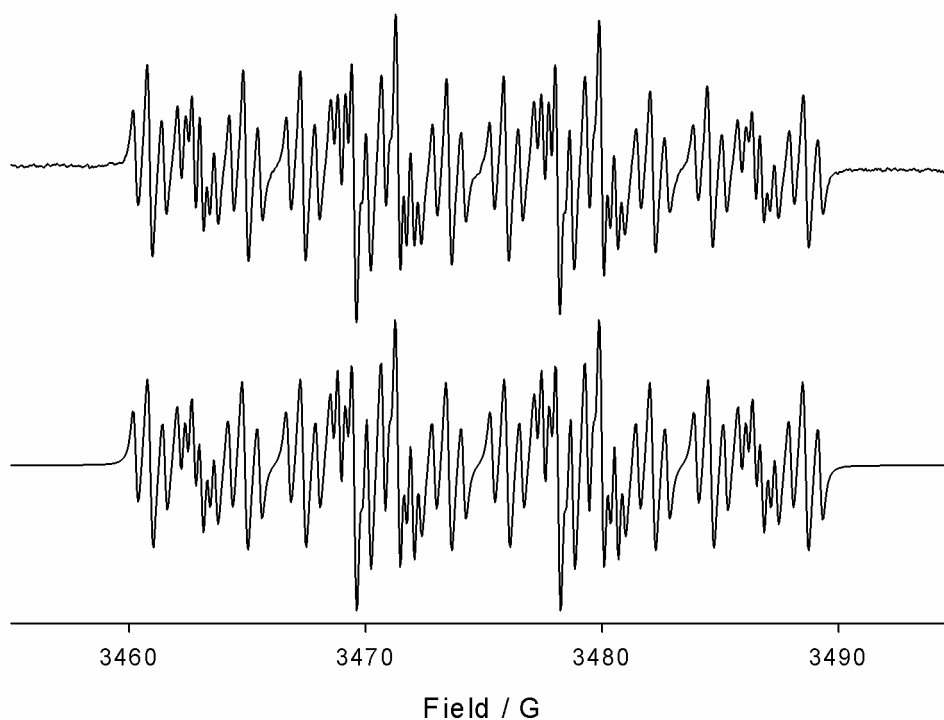


Figure S3. ESR spectrum (top) of the radical species electrogenerated from **7** (1 mM) in 0.1 M Bu₄NClO₄/CH₃CN at $E_{\text{appl}} = E_1^0$ and the corresponding theoretical simulation (bottom) obtained with the spectroscopic parameters reported in Table 1 in the manuscript.

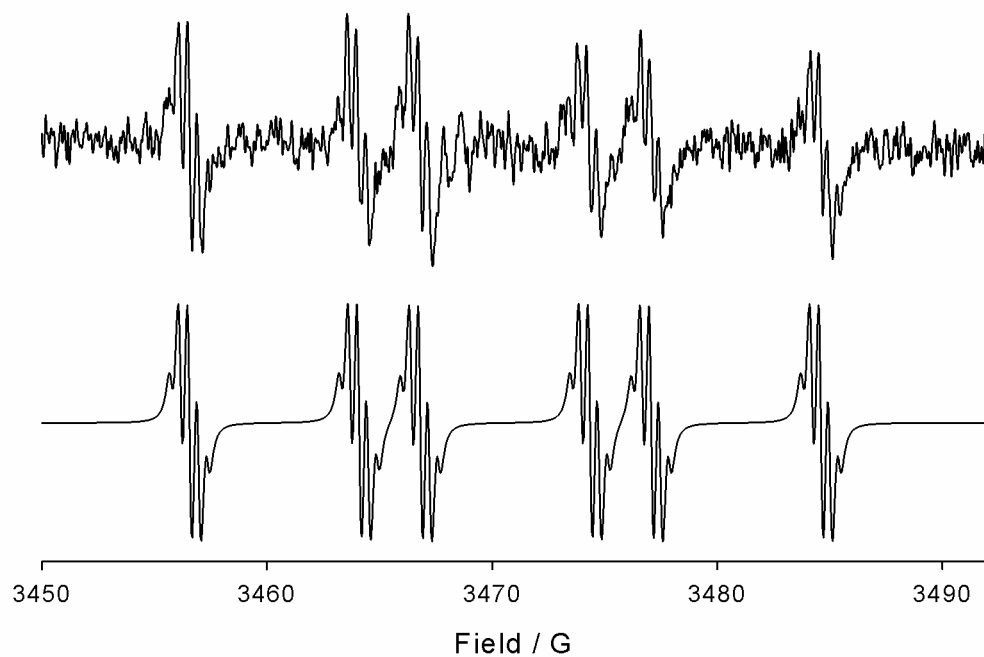


Figure S4. ESR spectrum (top) of the radical species electrogenerated from **8** (1 mM) in 0.1 M Bu₄NClO₄/CH₃CN at $E_{\text{appl}} = E_1^0$ and the corresponding theoretical simulation (bottom) obtained with the spectroscopic parameters reported in Table 1 in the manuscript.

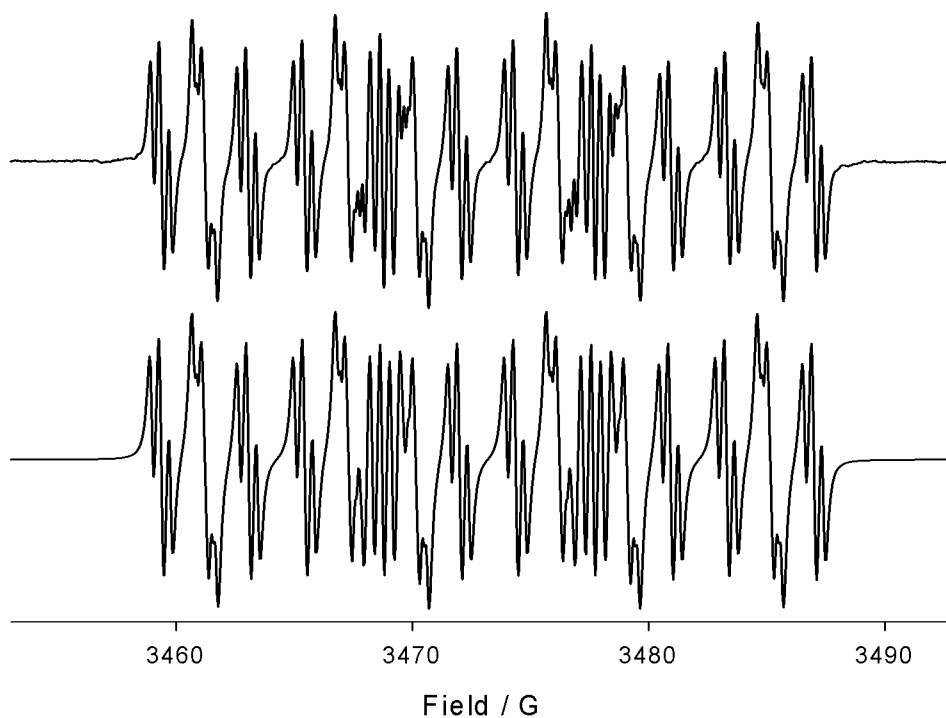


Figure S5. ESR spectrum (top) of the radical species electrogenerated from **9** (1 mM) in 0.1 M Bu₄NClO₄/CH₃CN at $E_{\text{appl}} = E_1^0$ and the corresponding theoretical simulation (bottom) obtained with the spectroscopic parameters reported in Table 1 in the manuscript.

Computational details. All the computations reported herein were performed with the Gaussian09²⁰ series of programs. The geometry of the various critical points was fully optimized with the gradient method available in Gaussian 09 at the DFT level using the nonlocal hybrid Becke's three-parameter exchange functional denoted as B3LYP²¹ and the 6-311++G(d,p) basis set.²² The solvent effects (acetonitrile, $\epsilon = 35.688$) were taken in account during optimization using the Polarizable Continuum Model (PCM) in the integral equation formalism variant (IEFPCM).²³ The solute cavity is built up using the UFF radii,²⁴ which places a sphere around each solute atom, with the radii scaled by a factor of 1.1. A computation of the harmonic vibrational frequencies was carried out to confirm the nature of each critical point. Isosurfaces spin densities were plotted using an isovalue of 0.004 ea_0^{-3} . The hyperfine coupling constants are calculated by single point calculation on the optimized geometry using the recently develop N07D²⁵ basis set for B3LYP

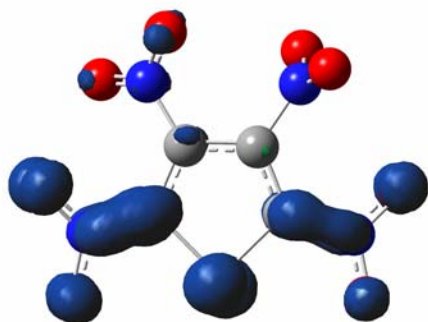


Fig S6. Isosurfaces spin densities plotted using an isovalue of 0.004 ea_0^{-3} for radical anion of tetranitrothiophene.

The geometry of the neutral molecule is characterised by the position of the 2 and 5 nitro groups, which are coplanar with the thiophene ring, while the 3 and 4-nitro groups have a dihedral angle tilted of about 60° from the plane of the thiophene ring.

DFT calculations show that for the radical anion of 2,3,4,5-tetranitrothiophene the spin density is mostly located between the nitro groups in position 2 and 5. Also the second electron is shared by the 2 and 5 nitro groups. In the dianion the closed shell structure is energetically favoured over the open one ($\Delta E_{\text{triplet-singlet}} = 4.2 \text{ kcal mol}^{-1}$).

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