Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2014

Immobilization of Helicene onto Carbon Substrates Through Electropolymerization of [7]Helicenyl-thiophene

J. Hrbac, J. Storch, V. Halouzka, V. Cirkva, P. Matejka, and J. Vacek

Section 1: Synthetic and Characterization Details

^{1}H and ^{13}C{1H} spectra were recorded using a 500 MHz instrument. Chemical shifts are reported in ppm (d) relative to TMS, referenced to the signal of $CDCl_3$ (δ = 7.26 ppm and δ = 77.23 ppm respectively). Electron impact (EI) mass spectra were determined at an ionising voltage of 70 eV. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF-Q III. TLC was performed on Silica gel 60 F254-coated aluminium sheets and compounds were visualized with UV light (254 nm). Commercially available reagent grade materials were used as received. Toluene was distilled from sodium under an atmosphere of argon. 9-Bromo[7]helicene was purchased from Lachner, Czech Republic.

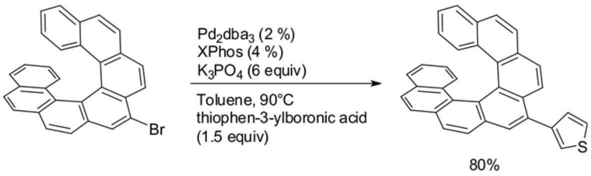

Fig. S1: Preparation of 3-([7]helicen-9-yl)thiophene.

3-([7]Helicen-9-yl)thiophene preparation is schematically shown in Fig. S1. Specifically, a Schlenk flask was charged with 9-bromo[7]helicene (250.0 mg, 0.55 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (11.3 mg, 10.9 µmol, 2 mol%), Xphos (10.4 mg, 22.0 µmol, 4 mol%), 3-thienylboronic acid (105 mg, 0.82 mmol, 1.5 eq) and K_3PO_4 (696 mg, 3.28 mmol, 6.0 eq). The mixture was heated at 90 °C for 15 h in toluene (15 mL) and then cooled to room temperature. The crude reaction mixture was filtered through a short pad of silica gel, eluting with toluene. The solvents were removed at reduced pressure and the crude product was purified by crystallization from the DCM/EtOH mixture, yielding the desired product (120.0 mg, 80 %) as a yellow powder with mp 189 – 192 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.19 (d, J = 8.5 Hz, 1H), 8.04 (s, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.74 (m, 2H), 7.60 (m, 1H), 7.57 (m, 1H), 7.54 – 7.48 (m, 3H), 7.33 (m, 2H), 7.17 (m, 2H), 6.94 (m, 2H), 6.48 – 6.42 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 140.9 (s), 133.3 (s), 131.69 (s), 131.68 (s), 131.2 (s), 130.8 (s), 130.7 (s), 130.5 (s), 130.0 (d+s, 2C), 129.5 (s), 129.3 (s), 128.24 (s), 128.20 (s), 127.8 (d), 127.5 (d, 2C), 127.2 (d), 127.15 (d), 126.7 (d), 126.58 (d), 126.56 (d), 125.8 (s), 125.7 (d), 125.5 (d), 125.4 (d), 124.9 (d), 124.88 (d), 124.5 (d), 124.46 (d), 124.2 (d), 124.16 (d), 123.7 (d), 123.6 (d) ppm. **EI MS:** 460 ($M^{+\bullet}$, 100), 445, 433, 419, 374, 230, 212, 205, 199, 187. **HR ESI MS:** calculated for $C_{34}H_{21}S$ (M+H) 461.1358, found 461.1358.

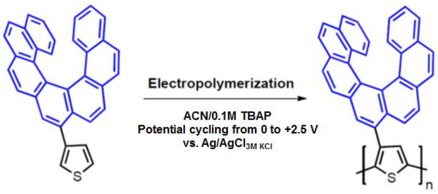

Fig. S2: Schematic representation of 3-([7]helicen-9-yl)thiophene electropolymerization.

Section 2: Electrochemistry and Electrosynthesis

Acetonitrile, p.a. (Sigma-Aldrich), tetrabutylammonium perchlorate - TBAP (Fluka), potassium ferricyanide (Lachema Brno, Czech Republic), hexaammineruthenium(III) chloride (Sigma) and thiophene (Sigma) were used for electrochemical experiments. Electrochemical measurements were performed using a CH-Instruments Model 660 C electrochemical workstation in three-electrode configuration. Ag/AgCl/3 M KCl was used as a reference electrode (RE-5B, BASi, Inc., U.S.A.), a platinum wire served as the auxiliary electrode and a glassy carbon disk electrode – GCE (3 mm in diameter, CHI104, CH Instruments, Inc. U.S.A.) and cylindrical carbon fiber electrode (CFE) were used as the working electrodes. Where appropriate, the GCE surface was (re)polished using an alumina slurry (0.05 µm) on a Microcloth pad (both Buehler, U.S.A.). CFE surface renewal was performed according to the published protocol (*Curr. Anal. Chem.* **2013**, *9*, 305-311). The electropolymerization process was implemented by immersing the GCE or CFE into an acetonitrile/0.1 M tetrabutylammonium perchlorate (ACN/TBAP) electrolyte containing 1 × 10^{-3} M 3-([7]helicen-9-yl)thiophene monomer (or thiophene and/or 9-bromo[7]helicene for control experiments). The electrode was then polarized from 0 to +2.5 V (vs. Ag/AgCl/3 M KCl) using cyclic voltammetry (10 cycles) at the scan rate of 100 mV.s^{-1} (if not stated otherwise). A schematic representation of the electropolymerization process for 3-([7]Helicen-9-yl)thiophene and the selectivity of the polymer to redox probes are shown in Figs. S2 and S3, respectively.

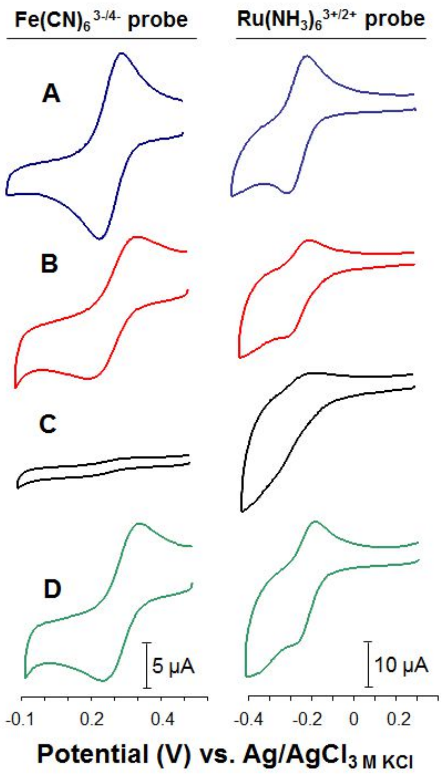

Fig. S3: CV records of 1 mM potassium ferricyanide **(left)** and hexaammineruthenium(III) chloride **(right)** recorded in 0.1 M KCl on **(A)** bare GCE and GCE modified by **(B)** poly(thiophene) or **(C)** poly[3-([7]helicen-9-yl)thiophene]. The 'electropolymerization' procedure was also performed with 9-bromo[7]helicene (Fig. S1, left) serving as the negative control **(D);** offset scale. GCEs were treated using the procedure as described in the previous paragraph (Section 2).

Section 3: Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained with a Tescan Vega 3 (SE image resolution 2 nm at 30 kV). The images were collected with a high voltage of 10 kV at a working distance ranging from 5 mm to 25 mm. The sample material (i.e. CFEs) was immobilized onto conductive carbon discs. The poly[3-([7]helicen-9-yl)thiophene] formation on the CFE surfaces is shown in Fig. S4. The effects of electropolymerization parameters as scan rate and number of applied cycles on deposit formation were tested as shown in Fig. S5. For evaluation of CFs thickness after electropolymerization software VegaTC (Tescan Brno, Czech Republic) was used.

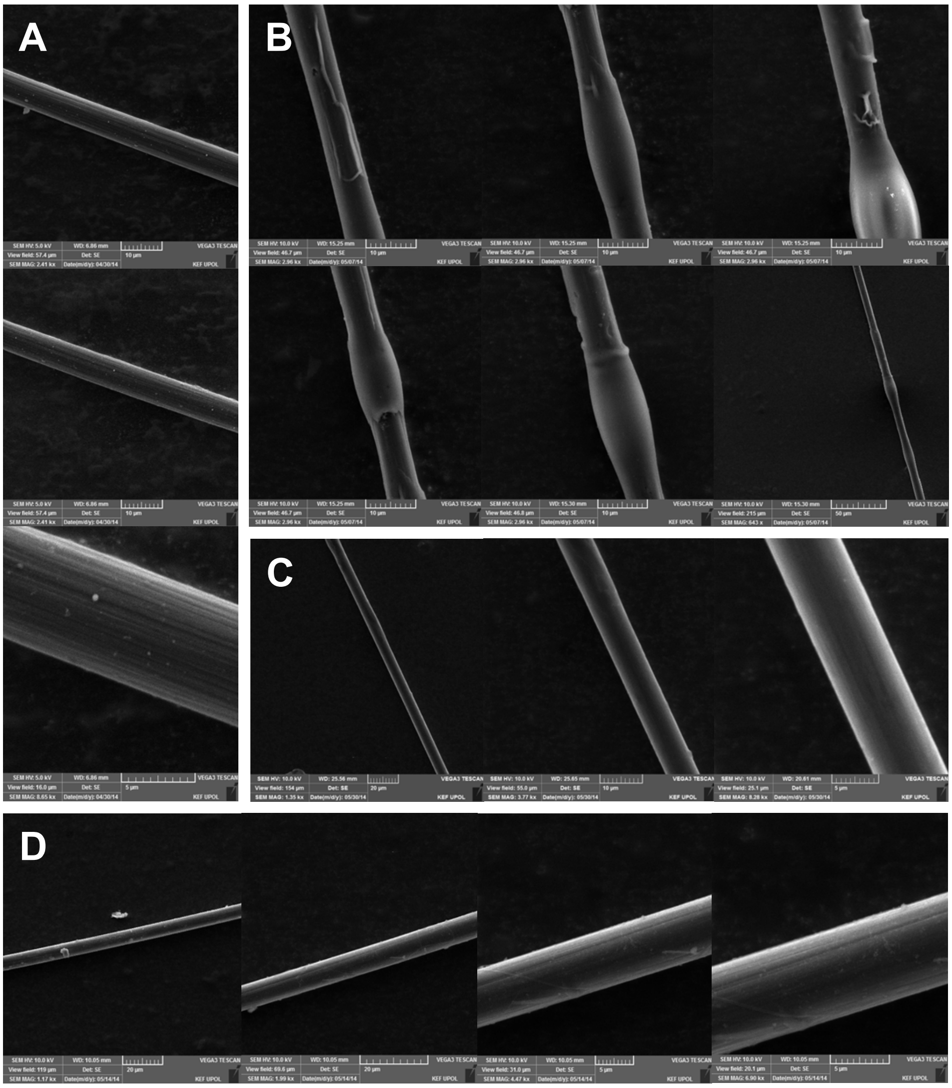

Fig. S4: Scanning electron micrographs of **(A)** bare CFEs, **(B)** poly[3-([7]helicen-9-yl)thiophene] coated and **(C)** poly(thiophene) modified CFEs. The practically same CF surface morphology as in panel C was found for CFEs after the ‘electropolymerization’ procedure with **(D)** 9-bromo[7]helicene serving as the negative control. The thickness of the poly[3-([7]helicen-9-yl)thiophene] layer is unequivocally higher than the poly(thiophene) layer under the same experimental conditions (Fig. S5).

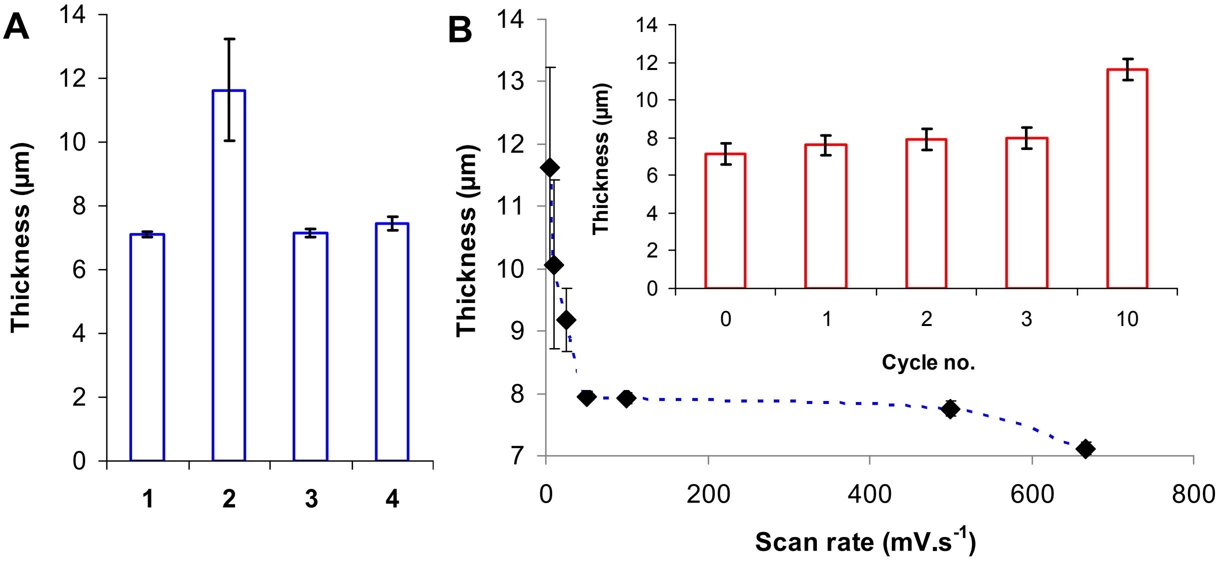

Fig. S5: Effect of electropolymerization parameters on the thickness of resulting CFs. **(A)** Thickness of bare electrode (1), and poly[3-([7]helicen-9-yl)thiophene] (2) and poly(thiophene) (3) modified electrodes. The 'electropolymerization' procedure was also performed with 9-bromo[7]helicene (4) serving as the negative control. **(B)** Dependence of thickness of CFs on scan rate and number of applied cycles (inset) used for electropolymerization of 3-([7]helicen-9-yl)thiophene. Electropolymerization conditions: 5 mV.s^{-1} (10 cycles) for A, 10 cycles for B and 5 mV.s^{-1} for inset in B. Data are means ± SD of six measurements. Error bars smaller than the plotted symbols are invisible. For other details, see Section 2.

Section 4: Vibrational spectroscopy

Fourier transform (FT) Raman spectra were recorded using an Equinox 55/S (Bruker, Germany) spectrometer equipped with an FRA 106/S Raman module (Bruker). Solid-state samples were irradiated with an Nd-YAG laser beam (1064 nm, Coherent, USA). 1024 scans were co-added to obtain the individual 2-cm^{-1}-resolved spectra. Twelve consecutively recorded spectra (laser power 50 mW) were averaged for 9-bromo[7]helicene and 3-([7]helicen-9-yl)thiophene, while 126 spectra (laser power 15 mW) were required to obtain a representative spectrum of the polymer. The intensities of all spectra were normalized using the software OPUS 4.0 (Bruker) and exported to ASCII-XY format. Fourier transform infrared (FTIR) spectra were collected using a Nicolet 6700 (Thermo Scientific) spectrometer equipped with a single-bounce attenuated total reflection (ATR) accessory MIRacle based on a ZnSe crystal. 256 scans were co-added to obtain the individual 2-cm^{-1}-resolved spectra. Two consecutively recorded spectra were averaged in all cases. The spectra were processed and normalized using the software Omnic 8.2 (Thermo Scientific) and exported to ASCII-XY format.

Both the Raman and infrared spectra of 3-([7]helicen-9-yl)thiophene monomer are dominated by the bands of the helicene moiety (demonstrated by the comparison with the spectra of 9-bromo[7]helicene). Nevertheless, the CH stretching vibrational modes of the thiophene ring are observed in the Raman spectra at 3105 cm^{-1} and 3089 cm^{-1}, while the CH stretching modes of helicene are located at ca. 3065 and 3049 cm^{-1}. Other evident Raman features of the thiophene ring are located at 1536, 1410, 1109 and 892 cm^{-1}.

The Raman spectrum of the polymer exhibits broadened characteristics, which correspond to a markedly disordered polymer layer. However, the spectral features of the helicene skeleton are usually observed at shifted positions, becoming comparable with nanocrystalline carbon or graphene-based materials (e.g. bands 1603, 1362, 1327 and 1213 cm^{-1}). The Raman characteristics of the poly(thiophene) moiety are relatively weak, but the positions are comparable with published data for substituted poly(thiphene)s, e.g. 1456, 1419, 1148, 972 and 760 cm^{-1}. The spectral features of the C-H stretching mode change significantly after electropolymerization; the CH modes of monomeric thiophene almost disappear, while the bands attributed to the helicene moiety shift to lower wavenumbers and become broader.

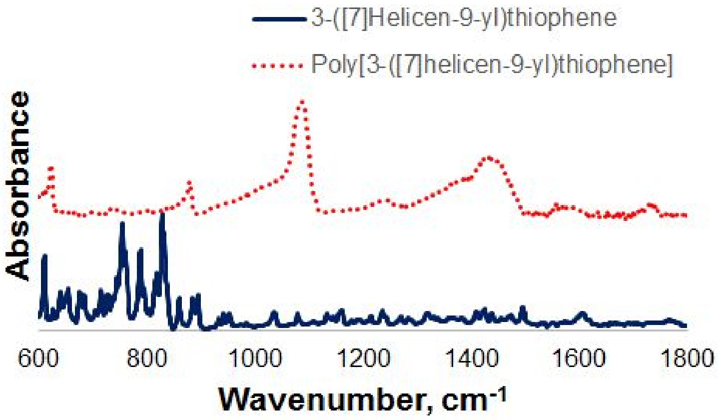

Fig. S6: Comparison of infrared spectra of polymer with 3-([7]helicen-9-yl)thiophene monomer (offset scale).

Similar observations are shown in the infrared spectra (Fig. S6). For the monomeric 3-([7]helicen-9-yl)thiophene, the CH stretching vibrations of the thiophene ring are observed at 3102 cm^{-1} and 3085 cm^{-1}, while the CH stretching modes of helicene are located at ca. 3045 and 3011 cm^{-1}. Similarly to the Raman spectra, the FTIR spectral features of the C-H stretching mode change significantly after electropolymerization; the CH modes of monomeric thiophene almost disappear while the bands attributed to the helicene moiety shift to lower wavenumbers and become broader. The FTIR spectrum of the polymer exhibits extremely broadened features, which correspond to a highly disordered polymer layer comparable to somewhat oxidized nanocrystalline carbon or graphene-based materials (e.g. bands 1733, 1575, 1436, 1377, 1238 and 1086 cm^{-1}) (*Phil. Trans. R. Soc. Lond. A* **2004**, *362*, 2425-2459; *New Developments in Photon and Materials Research, Joon I. Jang (Ed.), Nova Science Pub., ISBN: 978-1-62618-384-1* **2013**). However, the weak spectral features of the helicene skeleton are usually observed at slightly shifted positions.