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Chiral Carbon-rich Materials – From Single Molecule to Functional Layers

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Introduction. Helicenes are carbon-rich molecules with numerous of unique properties (e.g. semiconductivity, non-linear response, chiroptical properties), which make them attractive for application in material science, especially in thin films technologies. Such functional layers can be employed in a number of thin-layer operated devices (e.g. organic thin-film transistors, active organic light emitting layers or sensors). Going from single molecule to assembled layers lead as shown to a synergic enhancement of the additive properties beyond the sum of individual molecular properties. In addition, immobilization properties play also an important role in a functional layer fabrication. Therefore, a comprehensive study of two different carbon-rich materials properties – [6]helicene **1** and 1-butyl-3-(2-methyl[6]helicenyl)-imidazolium bromide **2** (Fig. 1) – and their thin films is presented. Because of different solubility, diverse preparation approaches had to be employed – electropolymerization and spin-coating. Spectroscopic and electrochemical properties were investigated along with examples of their practical use as detectors of biomolecules (e.g. DNAs).

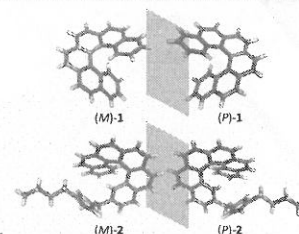


Fig. 1

Properties of 1. Helicenes are inherently chiral polyaromatic compounds comprised of all-ortho fused benzene rings making them nonplanar C_2 -symmetric helical polycyclic benzenoids. It is obvious that their extensive utilization in various areas of material sciences is foreseen, especially in optoelectronics. The purpose of the present work is to bring thorough electrochemical study of [n]helicenes which is of great interest in the context of optoelectronic and materials science applications. Concretely, racemic [5]-, [6]- and [7]helicenes were investigated electrochemically (Fig. 2a-c) and the results were supported by computational chemistry tools (Fig. 2d).

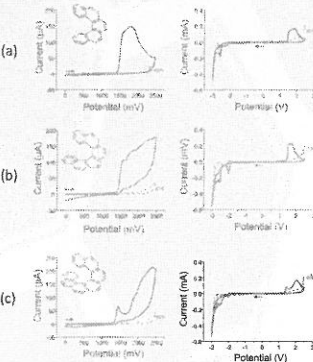


Fig. 2a-c: Anodic (left) and full (right) CV records of 1 mM [5]helicene (a), [6]helicene (b) and [7]helicene (c) at GCE in acetonitrile/0.1M TBAP electrolyte. CV parameters: scan rate 100 mV/s, E_{an} 0 V/ E_{cat} 2.5 V (for anodic records) and E_{an} 0 V/ E_{red} -3 V/ E_{cat} 2.5 V (for full scans), vs. Ag/AgCl/3 M KCl. Blank electrolytes (ele; highlighted by grey dashed lines) were deoxygenated by argon in case of full CV records.

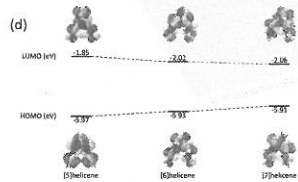


Fig. 2d: Calculated HOMOs and LUMOs energy levels for [n]helicenes (DFT calculations with B3LYP functional).

The electropolymerization of the helicenes opens new possibility for immobilization of helicenes onto solid supports. The polymeric layers were prepared on the ITO electrode and subjected to SEM characterization. The aim was to deposit compact layers with conducting properties which would find applications in optoelectronics and in the field of spectroelectrochemical sensing.

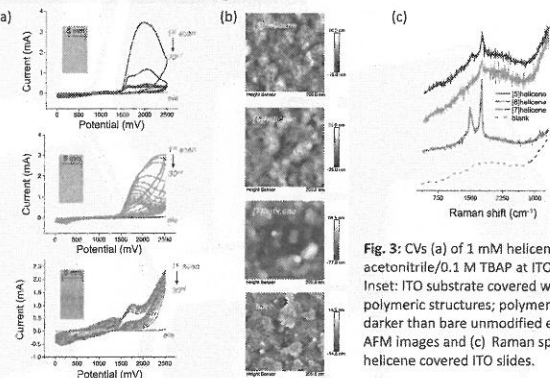


Fig. 3: CVs (a) of 1 mM helicenes performed in acetonitrile/0.1 M TBAP at ITO electrodes. Inset: ITO substrate covered with helicene polymeric structures; polymer-covered area is darker than bare unmodified electrode. (b) AFM images and (c) Raman spectra of bare and helicene covered ITO slides.

Layers were consequently analysed using Raman spectroscopy (Fig.3c) that confirmed typical D and G characteristics for sp^2 and sp^3 carbon materials [1]. The morphology of layers and their thickness of around 50 nm were revealed by AFM imaging (Fig. 3b) and elyptomically. It was found that helicene polymers are of isotropic nature and fully compact as confirmed using redox Fe/Ru markers [1]. Electropolymerization behavior was different between an individual helicenes, where the multi-spectral expertise resulted in the fact that [7]helicene undergoes redox transformation easily in comparison to the other compounds investigated. Electropolymerization involved by anodization at conductive (ITO) substrate opening new possibility to develop tailored strategies for immobilization of helicenes onto solid supports.

Properties of 2. To improve the solubility properties of helicenes in polar solvents let us to a development of rational design of helicene derivative **2** aiming its potential application. The imidazolium salt **2** [2] was immobilized onto SiO₂ substrate by spin-coating technique as a amorphous (Fig. 4a) or crystalline (Fig. 4b) deposit and used for the measurement of electrical performance.



Fig. 4: Schematic representation of the designed cell

The obtained electrochemical data clearly demonstrated the substantial increase in current for four orders of magnitude (from 3×10^{-10} to 2×10^{-6} A) under the constant voltage of -28 V in the temperature range from 30 to 160 °C. It is apparent from Fig. 5a (blue open symbols) that annealing the thin film at 190 °C improves the conductivity of the sample, especially at low temperatures. The annealed sample is mostly comprised of crystals (Fig. 4b), which overlap with each other and thus they create a connected path across the sample between the two gold electrodes. Furthermore, it has been shown that spincoated film of **2** can function as humidity detection device (Fig 5b).

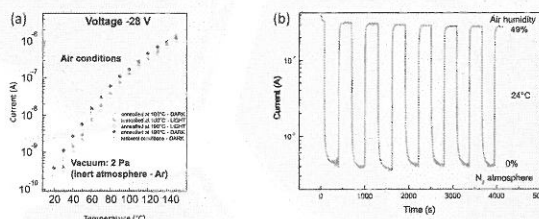


Fig. 5: (a) The annealed spincoated thin film of **2** dependence of current on temperature and (b) reversible current dependence on the air humidity at constant voltage (28 V) measured on crystalline thin film

These results encouraged us to fundamental study targeted interaction of **2** with diverse structural forms of single-stranded and double-stranded DNA using electrochemistry, gel electrophoresis and spectroscopic tools supported by molecular dynamics (MD) simulations (Fig. 6a). Both the experimental and theoretical work confirmed selective minor groove binding of **2** to DNA double-helical structure with maximal binding ratio 1 : 8 (**2** : base pairs) independently on the origin of DNA (Fig. 6b).

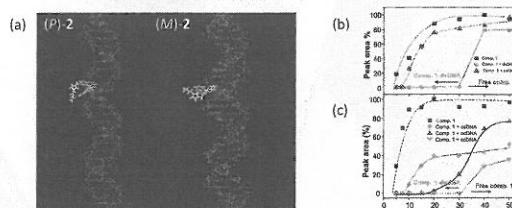


Fig. 6: (a) DNA double helix with **2** in the minor groove as the starting position for MD simulations. Electrochemical responses of free **2** and **2** in presence of (b) ss- and ds- oligonucleotide GC-53 and (c) ss-, oc- and ss- plasmid DNA (150 µg/ml; for all).

Compound **2** or its analogues could be applied for unique applications as development of multifunctional DNA structural probes based on selective minor groove binding, strong electrostatic attraction forces and chiral resolution by optically pure (P)-**2** and (M)-**2** enantiomers.

[1] R. L. McCreery, *Chem. Rev.* **2008**, *108*, 2646–2687.

[2] J. Storch, J. Zadny, T. Strasak, M. Kubala, J. Sykora, M. Dusek, V. Cirkva, P. Matejka, M. Krbal and J. Vacek, *Chem. Eur. J.* **2015**, *21*, 2343–2347.

