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Electrode Surface Modification by a Spirofluorene Derivative. An XPS and Electrochemical Investigation.

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Supplementary Information

Electrochemical instrumentation and measurements. Cyclic Voltammetry (CV) experiments were carried out in 0.05 M TBAH dichloromethane solutions in one-compartment electrochemical cell of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Viton O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Viton O-rings. The pressure measured in the electrochemical cell prior to perform the trap-to-trap distillation of the solvent was typically 1.0 to 2.0x10⁻⁵ mbar. The working electrode was a Pt disc (diameter: 125 µm) or a glassy-carbon disc electrode (diameter: 3 mm). The counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with respect to the ferrocene standard. $E_{1/2}$ values correspond to $(E_{pc}+E_{pa})/2$ from CV. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple.

Voltammograms were recorded with a AMEL Model 552 potentiostat controlled by either a AMEL Model 568 function generator or a ELCHEMA Model FG-206F. Data acquisition was

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performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda RL6 thermostat.

**Results and discussion**

CV experiments carried out in 1 solutions in ultra-dry dichloromethane evidenced that bulk films of 1 may also be obtained onto conducting substrates (platinum and glassy-carbon), by electrochemically-induced polymerization. Figure 1S shows the CV curves obtained in subsequent scans in the positive potential region, upon increasing the high potential limit. A peak corresponding to the one-electron reversible oxidation of 1 was observed with \( E_{1/2} = 0.98 \) V. At more positive potentials, the CV curve displayed an additional anodic peak which, from comparison with the first oxidation peak, can be estimated to comprise two subsequent two-electron oxidation processes, located at close potentials (\( E_p = 1.82 \) and 2.00 V) and only partly reversible. In fact, both the shape and the scan rate dependence of the cathodic peak observed in the reverse scan (at \( E_p = 1.70 \) V) are typical of adsorbed species (current \( \propto \) scan rate) and suggest adsorption of the product of multiple oxidation of 1 onto the electrode surface. Furthermore, subsequent scans between 0.0 and 2.1 V evidenced the gradual accumulation onto the electrode of an electroactive species responsible for the overall increase of current as shown in Figure 1Sa. Such a behavior was enhanced when potential was scanned up to larger potentials (Figure 1Sb) where the species undergoes a further oxidation process (with \( E_p = 2.05 \) V). All of the above suggests that, in line with previously reported electrochemical studies on spirobifluorene derivatives [Mattiello, L.; Rampazzo, L. *J. Chem. Soc., Perkin Trans.* 1993, 2, 2243; Mattiello, L.; Rampazzo, L. *Electroch. Acta* 1997, 42, 2257; Mattiello, L.; Fioravanti, G. *Synth. Commun.* 2001, 31, 89.], the multiple oxidation of 1 triggers its polymerization and the growth of a reversible and stable electroactive polymeric film onto the electrode surface. Further investigation aimed to the characterization of
electrochemical and, possibly, electrochromic properties of such electrochemically-active films is in progress.

Figure 1S

Figure 1S. Cyclic voltammetry curves recorded for 2-amino-9,9’-spirobifluorene in a 0.05 M TBAH dichloromethane solution upon increasing the high potential limit from a) to b).