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A facile route to steady redox-modulated nitroxide spin-labeled surfaces based on diazonium chemistry†

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A TEMPO derivative was covalently grafted onto carbon and gold surfaces *via* the diazonium chemistry. The acid-dependent redox properties of the nitroxyl group were exploited to elaborate electro-switchable magnetic surfaces. ESR characterization demonstrated the reversible and permanent magnetic character of the material.

Nitroxides have found widespread use for oxidative transformations in organic synthesis, controlled preparation of functional polymers, resolution of reaction mechanisms or metabolism in radical (bio)chemistry and as building blocks to prepare organic magnets in material chemistry.[1] In all cases, nitroxides act either as persistent radicals, radical traps or spin probes.

Due to their unique reactivity, free-radical nitroxyls were made popular for the conversion of an external stimulus into a magnetic output[2–4] and efforts were made to extend their chemistry in solution toward surfaces.[5–9] Recently, reversible photo-responsive π-conjugated organic systems functionalized with nitroxyl radical centers at both ends have been proposed for switching their magnetic properties in solution by a change in the molecular environment between the two radical centers.[10,11] These fascinating results offer great potentialities for achieving read/write organic memory devices, but the preparation and the attachment of such stimuli-responsive molecules are bottlenecks in the production of a switchable magnetic surface.

To simplify the reaction work-up and for improving the processability of magnetic surfaces, Rovira and coworkers proposed the use of polychlorotriphenylmethyl and tetrathiafulvalene electroactive organic radicals as switching functions.[12,13] For storage and memory applications, the charge stored in the discrete redox states must be preserved for long times when no potential is applied (*i.e.* long charge-retention time is required).[14] Recently, Bocian and Lindsey *et al.* have shown that the kinetics of charge dissipation parallels the kinetics of the electron transfer.[15] With this viewpoint, the choice of the redox center and the strategy used for attaching the molecule at surfaces are crucial so that the memory storage element is viable.[16]

Here, we suggest benefiting from the remarkable acid-dependent redox properties of nitroxides[17–19] (*i.e.* acid-catalyzed disproportionation and the possibility of reverse comproportionation reaction) (1) reconsidering the diazonium chemistry as a flexible and robust methodology to prepare nitroxide-tethered surfaces and (2) permitting the preparation of electro-switchable surfaces that change the magnetic properties between the permanent diamagnetic and paramagnetic states.

Because of their ability to trap free-radicals, radical-induced procedures are not amenable to the attachment of nitroxides at surfaces because the grafting by radical attack is short circuited by coupling reaction with nitroxides.[20] So, in this work we exploited the disproportionation of the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical into oxoammonium and hydroxylamine under acidic conditions to prepare the non-radical hydroxylamine form of diazotated *N*-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-aminobenzamide (Scheme 1).[21]

The resultant diazonium salt can be considered as a hybrid molecule connecting a diazonium function, reducible to a reactive aryl radical, with the protected form of a stable nitroxyl group. Glassy carbon (GC) and gold working electrodes were modified by recording 10 cyclic voltamograms at 50 mV s^{-1} between 0.5 and −0.8 V *vs.* Ag|Ag^+ in a HCl–acetonitrile mixture (4/96, v/v) containing 1 mM ABzTEMPO in the presence of 3 equivalents of $NaNO_2$. Strong passivation of the electrodes was observed (ESI,† Fig. S1) in accordance with the grafting process. Under such conditions, hydroxylamine-tethered electro-switchable magnetic surfaces were obtained. The modified surfaces were examined using X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) and their magnetic properties were examined using electron paramagnetic resonance (EPR).[22]

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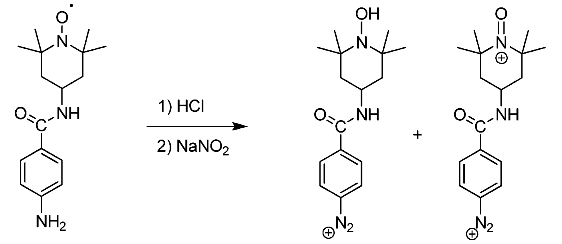


Scheme 1 Disproportionation and diazotization of *N*-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-aminobenzamide (ABzTEMPO).

Fig. 1 (top) shows CV recorded at a modified GC electrode. At the first scan, no redox wave is observed. This observation agrees with the absence of EPR response recorded for the modified surface, confirming that the grafted molecules are not in their radical form. However, the presence of the hydroxylamine form is proved by the intense XPS peak localized at 399.6 (ESI,† Fig. S2). When repetitive cycling is applied, a reversible system attributed to the nitroxide/oxoammonium cation redox couple is progressively restored. Note that similar behaviour is observed using a gold electrode (ESI,† Fig. S3). After thirty cycles, the current peak intensity reaches a maximum. The integration of the voltammetric signal gives a surface coverage of 2.1×10^{-10} mol cm^{-2}, which corresponds to less than a close-packed monolayer calculated for such structure (4.6 to 5×10^{-10} mol cm^{-2}).[23]

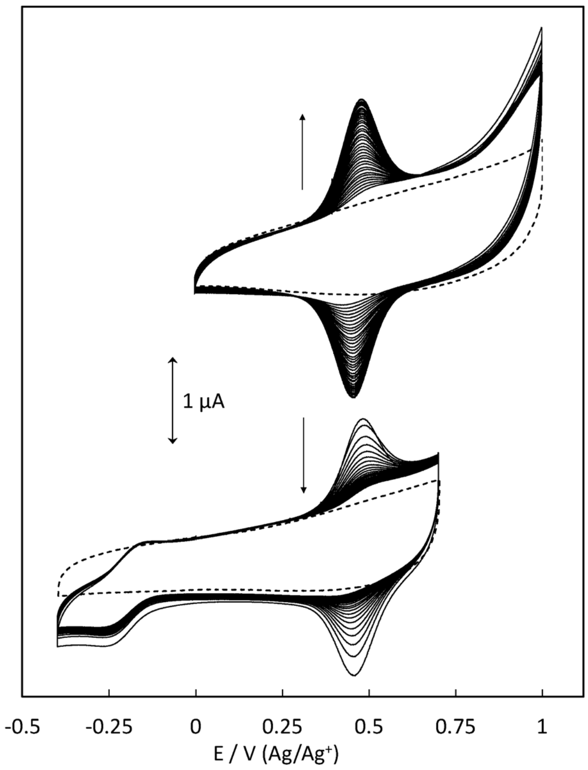


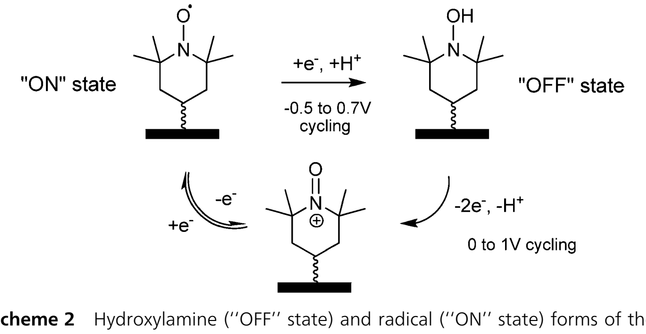
Fig. 1 (top) Repetitive CVs obtained in acetonitrile + 0.1 M Bu4NPF6 with a modified glassy carbon electrode prepared in protic medium. (bottom) Repetitive CVs recorded in acetonitrile + 0.1 M Bu4NPF6 onto a modified glassy carbon electrode previously oxidized to restore the nitroxide/oxoammonium cation redox couple. Scan rates: 50 mV s^{-1}. Dashed lines correspond to the CVs of bare electrodes.

To explain this behaviour, it can be postulated that the hydroxylamine form (>N–OH) is oxidized to the oxoammonium cation (>N$^+$=O) by potential cycling.[18] So, as the hydroxylamine-tethered surface is converted into the oxoammonium-tethered surface, the >N–O/>N$^+$=O couple is progressively restored. This hypothesis is supported by the fact that no reversible system can be restored under repetitive potential cycling below +0.7 V. Note that the hydroxylamine oxidation peak cannot be visualized in our experiment, but compared to the response of an unmodified glassy carbon electrode, a supplementary current emerges, which can be attributed to the reaction. The cycling appears to be necessary to obtain a complete transformation of hydroxylamine into the oxoammonium cation.

Because >N$^+$=O/>N–OH and >N–O/>N–OH redox couples are strongly irreversible,[17] it provides a unique opportunity to switch on–off the immobilized reversible system at +0.43 V (*i.e.* by oxidizing the initial hydroxylamine form into the oxoammonium cation or by reducing the nitroxyl radical to the hydroxylamine (scheme 2)).

Fig. 1 (bottom) shows the repetitive voltammetric cycling of the modified electrode over a more cathodic range, including a reversible electrochemical system centered at −0.2 V. The comparison with the response of a freshly polished carbon electrode confirms that this reversible system is due to the modification of the surface. The understanding of the electrochemical process occurring at this potential appears to be complex. This system could not directly correspond to the mono-electron reduction of the nitroxyl form to hydroxylamine (due to the reversibility and peak intensity) but is undoubtedly linked to its formation. Indeed, the voltammetric cycling allows us to switch off the redox signal at +0.43 V, which was restored previously. Further experiments will be dedicated to the comprehension of this point.

The EPR responses as a function of the oxidation state of the TEMPO layer are presented in Fig. 2. At the ''ON'' state (for the nitroxyl-tethered carbon surface), the classical hyperfine splitting due to coupling of the unpaired electron with nucleus 14N is obtained. The *g* value, equal to 2.006, is consistent with previous reports on immobilized nitroxyl radicals.[24] EPR measurements show that the paramagnetic character of the molecules linked to the surface is permanent. It is noteworthy that no change in the signal was detected 24 h after the nitroxyl form was restored. Conversely, no EPR signal is obtained when the reversible system completely disappears by recording CVs



Scheme 2 Hydroxylamine (''OFF'' state) and radical (''ON'' state) forms of the modified surface obtained after appropriate cycling.

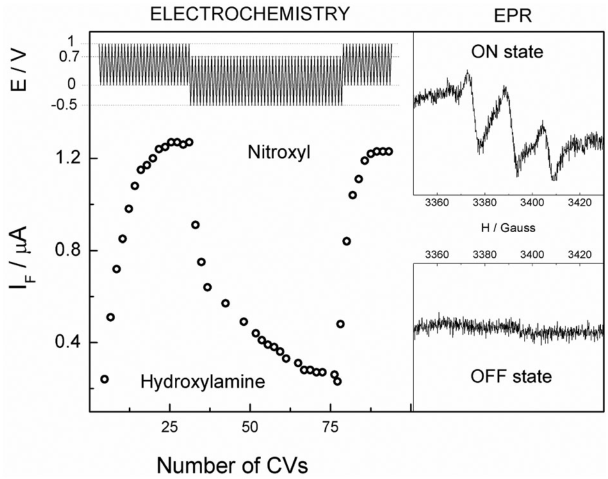


Fig. 2 Evolution of the anodic peak current measured at +0.47 V when the potential is cyclized between 0 and +1 V for transforming the hydroxylamine into the radical nitroxyl or from +0.7 to −0.5 V to reduce the radical nitroxyl to the hydroxylamine. Inset OFF state: the EPR signal after cycling between 0.7 and −0.5 V. Inset ON state: the EPR signal after cycling between 0 and 1 V.

in the nitroxyl/hydroxylamine potential window. The decrease in the peak current after 2 switches corresponds to 20% of the total activity recorded after the first switch "on".

In the first place, the reversible redox system can serve as a switching function between the positively charged oxoammonium cation and stable nitroxyl radical. In the second place, the combined use of the two kinetically slow redox couples $>N^+{=}O/{>}N{-}OH$ and $>N{-}O/{>}N{-}OH$ allows easy access to the stable nitroxyl radical or neutral hydroxylamine form capable to be maintained for an extended period even in the absence of applied potential. This kind of electro-switchable magnetic surface presents interesting potentialities for storage and memory applications.

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21 Synthesis of *N*-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-aminobenzamide (AbzTEMPO). The synthesis consists of peptide coupling between 4-aminoTEMPO and 4-aminobenzoic acid achieved in three steps: protection, coupling and deprotection. First, 4-aminobenzoic acid is protected by fluorenylmethyloxycarbonyl chloride, according to the procedure described previously by Carpino and co-workers.[25] Then the protected acid is coupled with 4-aminoTEMPO in the presence of dicyclohexylcarbodiimide/*N*-hydroxybenzotriazole, and finally, deprotection is carried out by piperidine to obtain AbzTEMPO (47%). See ESI† for detailed synthesis and characterization.
22 Characterization of the modified surfaces. XPS experiments were performed on gold surfaces prepared by physical vapor deposition of an adhesion layer of chromium on glass covered with a 100 nm layer of gold. EPR characterizations were carried out on a BRUKER EMX spectrophotometer operating at room temperature and at a frequency of 9.524124 GHz with a modulation amplitude of 2.5 G and 20 mW. Experiments were performed at room temperature using a modified 0.5 mm diameter gold (99.99%) wire inserted into a quartz cell. Cyclic voltammetric measurements were performed in a three-electrode cell. The working electrode consists of a glassy carbon or gold disk purchased from Bioanalytical Systems (models MF-2012 and MF-2014, respectively). A platinum wire was used as a counter electrode and potential values were reported *versus* an Ag|AgCl (saturated KCl) reference electrode. A potentiostat/galvanostat model VMP3 (from Bio-Logic) monitored using ECLab software was used for the electrochemical experiments.
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