

Supporting information

Efficient covalent capping of carbon and gold with TEMPO for catalysis and spin writing

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References and notes

† 4-Hydroxy-2,2,6,6-tetramethylpiperidine (0.4 g, 2.5 mmol) in 5 mL of anhydrous THF was added to NaH (0.066 g, 3.75 mmol) under Ar atmosphere. The mixture was stirred for 30 min, then 1-bromo-6-chlorohexane (0.54 g, 2.7 mmol) was added dropwise. Stirring was continued for 24 h at 65 °C under argon. Sodium bromide was then filtered off and THF was evaporated. The crude product was washed with 5 mL of water, then extracted with 2×5 mL of diethyl ether. After drying the organic phase over MgSO₄, the obtained 4-(6-chlorohexyl)-2,2,6,6-tetramethylpiperidine (0.58 g, 2.2 mmol) was subjected to Cl/I displacement with NaI (0.32 g, 2.2 mmol) in 5 mL of anhydrous acetone at 50 °C for 2 days to give the iodoethyl derivative in 85.5 % yield (0.66 g, 1.88 mmol).

¹H NMR (300 MHz, CDCl₃, δ/ppm): 0.83-0.90 (4H, m, CH₂); 1.04-1.15 (2H, m, CH₂); 1.18-1.23 (2H, m, CH₂); 1.26 (12H, s, CH₃); 1.37-1.47 (2H, m, CH₂); 1.53-1.60 (2H, m, CH₂); 1.79-1.88 (2H, m, CH₂); 1.93-1.98 (1H, m, NH); 3.19 (1H, m, CH) 3.44-3.51 (2H, m, CH₂). ¹³C NMR (75 MHz, CDCl₃, δ/ppm): 7.08, 28.72, 29.07, 30.23, 31.75, 34.67, 35.01, 48.17, 51.57, 64.43, 72.5. MS, m/z: 352 (M⁺, 100); 224 (32); 124 (57); 98 (21); 58 (20); 41 (22).

‡ 0.5 mol L⁻¹ K₂CO₃ in 25% H₂O₂ (see [1]). The oxidation is very rapid and only takes 20 s; shorter times lead to incomplete N-H to N→O conversion whereas longer (>1-2 min) treatment causes deterioration of the grafted interface. It is critical to keep the interface wetted with the solvent for once dried, the (CH₂)₆ linkers collapse and would not redress upon soaking with another solvent (CH₃CN, acetone, hexane).

A permanent switching between para- and diamagnetic states (nitroxyl radical >NO[•] and its hydroxylamino form >NOH, respectively) of TEMPO immobilized on the GC via a rigid aryl-peptide scaffold was reported [2] to be achieved after 30 voltammetric cycles, exploiting chemical irreversibility of N=O⁺/NOH and NO[•]/NOH redox systems. In contrast to this system, the ET kinetics of the pure TEMPO⁺/TEMPO redox pair (in solution: k_s ≈ 0.02 cm s⁻¹ [3]; grafted at Au nanoparticles: 106-165 s⁻¹ [4] or 20-50 s⁻¹ [5] depending on the linker used) is fast, comparable to that of ferrocene [6], it is electrochemically reversible [7] and chemically stable since it does not involve any chemical step as in the quasi-reversible NO[•]/NOH electrochemical regeneration of the nitroxyl radical.

The proposed in the present communication method of TEMPO immobilization allows a dynamic spin-switching based on a pure TEMPO⁺/TEMPO Nernstian system without any chemical steps involved. The presence of a flexible (CH₂)₆- linker creating a surface-attached pseudo-diffusional layer ca. 14 Å thick improves the shape of its current (I - t) and EPR responses.

¶ In aqueous media (pH 10), the observed catalytic feature is more complex (Fig. S6). We tentatively rationalize it as a one-electron reductive cleavage of the N-O(CH) bond in the >N⁺(OH)OCHPh intermediate yielding TEMPO-OH and PhCHO^{-•} anion radical (produced much before the potential of its “normal” formation, E_p(PhCHO) < -1.4 V [8]) so that the oxidation current of the latter sums with the reduction current of hydroxylamine (Fig. S5); these processes compete on the remaining part of the cathodic scan causing a characteristic zero-current crossing on the voltammogram (Fig. S6). The mechanism of catalysis by grafted TEMPO in this system thus seems to be more complex than the one postulated for the homogeneous process [9] and generally accepted in the later papers [10-14]; as was stated in a recent paper, in spite of the synthetic progress in this field, the “aspects of the mechanism of the TEMPO mediated electrochemical oxidation of alcohols remain unclear” [15].

On the other hand, bare Au/AuO interfaces are also known to catalyse alcohol oxidation [16,17], though thick hydrophobic grafted layer (>13 Å for (CH₂)₆, at 4 kohm resistance, EIS Fig. 3E) supposedly prevents the accumu-

lation of OH⁻ anions from an aqueous solution at the metal surface to onset the formation of the superficial gold oxide and to render the AuO catalysis effective. In fact, it was reported that even the presence of ClO₄⁻ anion efficiently inhibits the alcohol oxidation at an otherwise non protected bare gold interface [17]. With this, the oxide role in this process was questioned [18] so that there might be a possibility of a base-catalysed first step of oxidation at the outer (TEMPO-capped) side of the grafted interface with the following diffusion of the alkoxide intermediate through the hydrophobic layer to the metal where second, metal-catalysed, step might occur. Whichever the case, some interference from Au or AuO that might be formed on the electrode surface through the defaults in the grafted hydrophobic layer cannot be entirely ruled out; obviously, an additional detailed study is needed in order to rationalize this complex issue.

References

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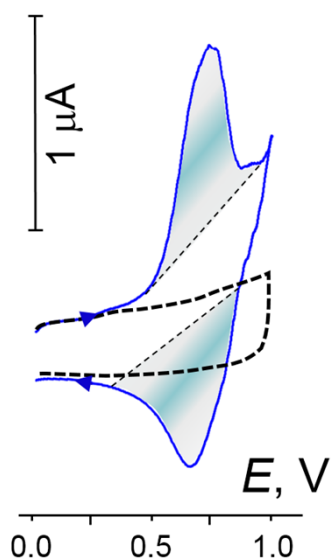


Fig. S1. Voltammetry of TEMPO immobilized at a Pt electrode following the similar procedure (grafting of $\text{TMP-O}(\text{CH}_2)_6\text{I}$ by means of 12 consecutive scans from 0 to -1.5 V in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 , $\nu = 50$ mV s^{-1} , followed by $\text{H}_2\text{O}_2/\text{K}_2\text{CO}_3$ oxidation of grafted TMP to TEMPO). $T = 293$ K. The shadowed zones show current integration of $\text{TEMPO}^+/\text{TEMPO}$ redox pair. Dotted curve is the response of the same electrode after polishing off the grafted layer (ca. $0.05\text{-}0.1$ μm) with Struers 1200 paper.

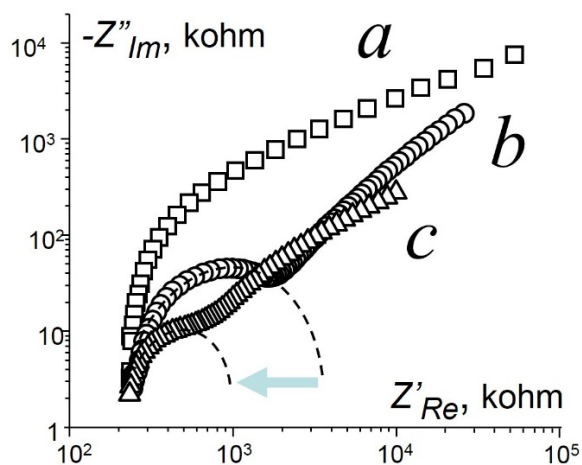


Fig. S2. Nyquist plots for first one-electron reduction step of chloranil ($E_0 = -0.1$ V vs. SCE) in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 at: (a) bare GC electrode, (b) same GC electrode with grafted $(\text{CH}_2)_6\text{O-TMP}$ layer, (c) the same electrode as in (b) after dipping into 0.1 M HCl (corroborating the protonation of the grafted amino groups to form a polar $-(\text{CH}_2)_6\text{O-TMP}\cdot\text{HCl}$ interface). The arrow shows the three-fold decrease in charge transfer resistance of the protonated layer indicating the increase in ET rate through this more polar ionic interface. Frequency range from 242 kHz to 0.1 Hz. $\Delta E = 10$ mV.

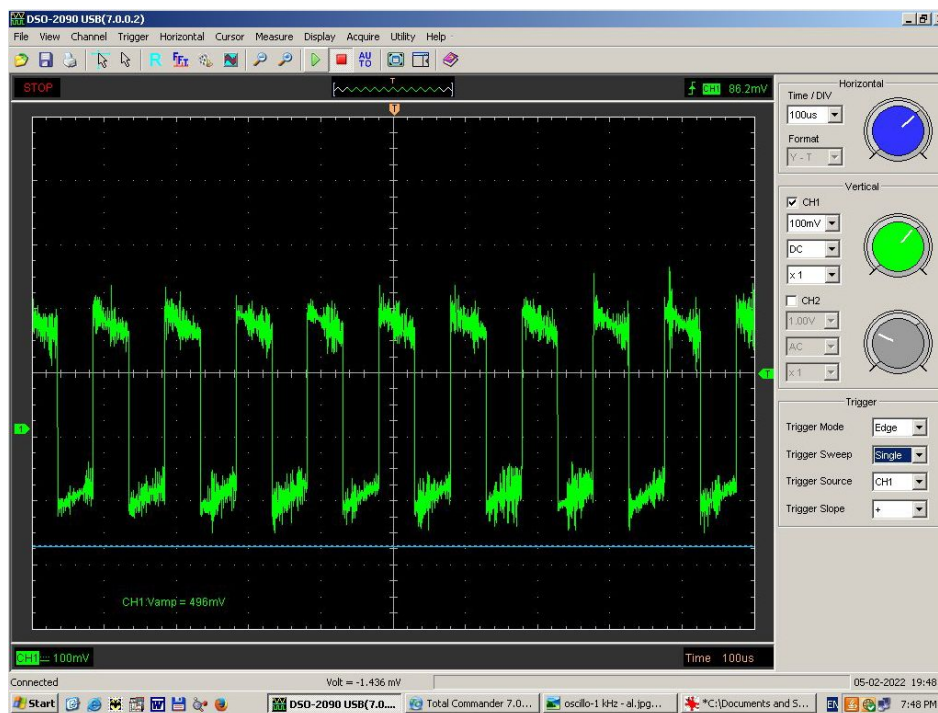


Fig. S3. Oscillogram of the current response ($I - t$) of TEMPO⁺/TEMPO redox system (CH₂)₆-grafted onto graphite. CH₃CN/0.1 M Bu₄NPF₆. Square-wave (two-step) polarization: E₁ = 0.5 V, E₂ = 0.9 V. Frequency 10 kHz. At this frequency, the polarization during 10 s corresponds to 10⁵ unitary cycles in the two-step potentiostatic chronoamperometry.

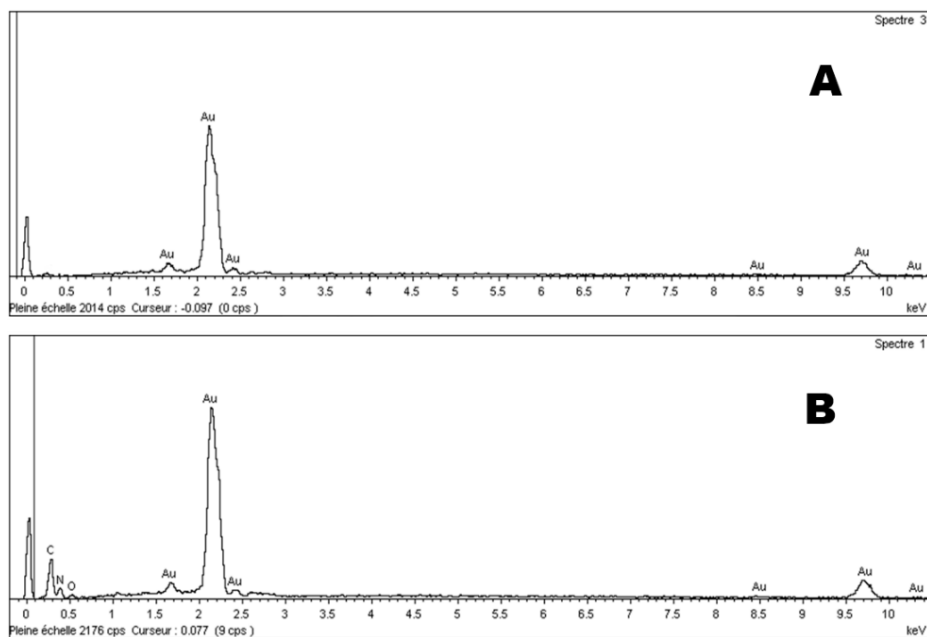


Fig. S4. EDS analysis of the atomic composition of the gold interface: (A) pristine gold plate before grafting, (B) same interface after covalent immobilization of TEMPO attesting to the presence of C, N and O atoms. The analysis was performed at a SEM JEOL JSM 7100F (EDS, EBSD) apparatus at CMEBA (Centre de Microscopie Électronique à Balayage) of the University of Rennes 1.

