Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Facile Route to Redox-Modulated Nitroxide Spin-Labeled Surfaces Based on Diazonium Chemistry.

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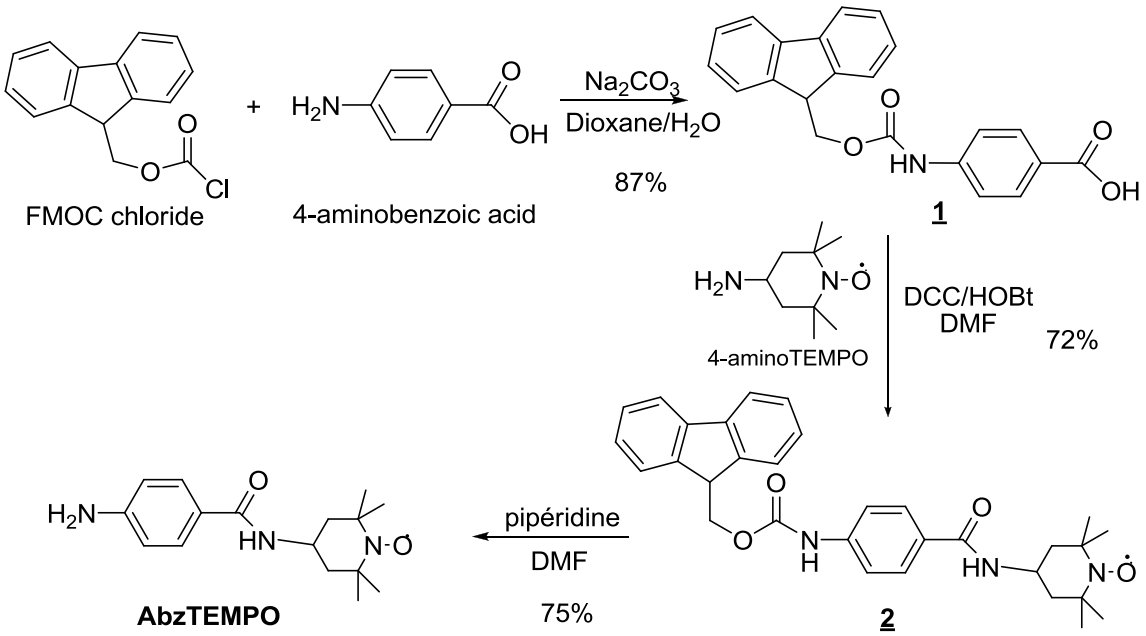
Reagents and Instrumentation

Starting materials, reagents and solvents were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kiselgel 60 F_{254} 0.2 mm thickness precoated TLC plates, which were inspected by UV-light. Column chromatography was performed using Acros Organics Kiselgel 60 (0.040–0.060 mm, 230–240 mesh ASTM). ^{1}H and ^{13}C NMR spectra were recorded on a Brüker 300 MHz spectrometer. MS analysis was performed on an ESI/APCI Ion Trap Esquire 3000+ from Brüker. IR spectra were recorded on a Brücker Vertex 70 spectrophotometer and melting points on a Kofler bench.

Synthesis of aminobenzenetetramethylpiperidine-N-oxyl (ABzTEMPO).

Synthesis of *N*-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-aminobenzamide (AbzTEMPO) consist on a 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 procedure previously described by Carpino and co-workers (ref : L.Carpino and G. Y. Han, *J. Org. Chem.* **1972**, 37, 3404-3409), then the protected acid is coupled to 4-aminoTEMPO in presence of dicyclohexylcarbodiimide/N-Hydroxybenzotriazole, and finally, deprotection is carried out by piperidine to give AbzTEMPO (47%).



4-(9H-fluoren-9-ylmethoxycarbonylamino)benzoic acid ***1*** : 566 mg (2.19 mmol, 1 eq.) of fluorenylmethyloxycarbonyl (FMOC) chloride in 5 mL of dioxane is added dropwise to 10 mL of distilled water cooled at 0-5°C and containing 300 mg (2.19 mmol, 1 eq.) of 4-aminobenzoic acid and 580 mg of Na_2CO_3. After stirring at 0-5°C for 15 min and then at room temperature for 3 hours, 150 mL of water are added. The mixture is extracted with 100 mL of diethyl ether. After acidification of the aqueous layer with 6 M HCl to Congo red paper, the precipitate is filtered, washed with water and then dried *in vacuo* during several days at 45°C. Compound **1** is obtained in 87% yield (683 mg) as a white powder.

^{1}H NMR (DMSO): δ 10.05 (s, 1H, COOH), 7.92 (d, 2H, ortho CO_2H), 7.84 (d, 2H, ortho NH(C=O)), 7.75 (d, 2H, H_{arom} Fmoc), 7.54 (d, 2H, H_{arom} Fmoc), 7.43 (t, 2H, H_{arom} Fmoc), 7.36 (t, 2H, H_{arom} Fmoc), 4.53 (d, 2H, CH_2-CH), 4.33 (t, 1H, CH-CH_2). ^{13}C NMR (DMSO): δ 167.5, 153.8, 144.2, 143.7, 141.3, 130.9, 128.2, 127.6, 125.6, 125.0, 120.7, 117.9, 66.3, 47.1. ESI-MS: calculated for $C_{22}H_{17}NO_4$ 359; found: +MS $[M+Na]^+$ 382; -MS: $[M-H]^-$ 358, $[M+Cl]^-$ 394, $[2M-H]^-$ 717. IR (ATR) cm^{-1}: 3347, 2971, 1709, 1674, 1610, 1526, 1410, 1312, 1222, 1052, 850, 737. Mp > 240°C.

N-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-(9H-fluoren-9-yl-methoxycarbonyl amino)benzamide ***2*** : 343 mg (2.00 mmol, 1.2 eq.) of 4-aminoTEMPO solubilized in 4 mL of DMF is added to 15 mL of anhydrous DMF containing 600 mg (1.67 mmol, 1 eq.) of **1**. After the mixture is cooled at 0-5°C with an ice-water bath and deoxygenated with nitrogen, 339 mg (2.51 mmol, 1.5 eq.) of N-Hydroxybenzotriazole (HOBt) and 517 mg (2.51 mmol, 1.5 eq.)

of dicyclohexylcarbodiimide (DCC) are added. After stirring at 0-5°C for 1h and then at room temperature for 48h, 40 mL of AcOEt are added and the solution is filtered over cotton. After washing with water, the organic layer is dried over $MgSO_4$, filtered and concentrated under vacuum. The red residue obtained is purified by chromatography on a silicagel column (Eluent: CH_2Cl_2/AcOEt 8/2). Compound **2** is obtained in 72 % yield (616 mg) as a pink orange powder.

^{1}H NMR ($CDCl_3$): δ 7.81 (d, 2H, H_{arom} Fmoc), 7.63 (dp, 2H, H_{arom} Fmoc), 7.44 (t, 2H, H_{arom} Fmoc), 7.35 (t, 2H, H_{arom} Fmoc),7.85-7.30 (bs, 4H, H_{arom} benzo), 4.61 (d, 2H, CH_2 Fmoc), 4.31 (t, 1H, CH Fmoc), 1.80-1.20 (bm, H TEMPO). ^{13}C NMR ($CDCl_3$): δ 171.2, 153.1, 143.6, 141.5, 140.0, 128.1, 127.4, 125.3, 120.3, 67.3, 60.6 47.2, 34.2, 29.8, 25.8, 25.1, 21.3, 14.4.
ESI-MS: calculated for $C_{31}H_{34}N_3O_4$ 512; found: +MS $[M+2H]^+$ 514, -MS $[M+Cl]^-$ 547, $[2M+Cl]^-$ 1059. IR (ATR) cm^{-1}: 3276, 3031, 2974, 2938, 1696, 1625, 1526, 1317, 1236, 1088, 1050, 853, 737. Mp = 164-166°C

ABzTEMPO (ou N-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-4-aminobenzamide): To a solution of 550 mg (1.07 mmol, 1 eq.) of **2** in 8 mL of DMF are added 0,45 mL of piperidine (~4,5 mmol, 4 eq.). After stirring at room temperature for 1h, the orange solution is pooled into 120 mL of cold water. The white precipitate is removed by filtration and the filtrate is extracted five times with 100 mL of diethyl ether. The organic layers are combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue is purified by chromatography on a silicagel column (Eluent: CH_2Cl_2/MeOH 96/4). AbzTEMPO is obtained in 75% yield (236 mg) as an orange powder.

^{1}H NMR ($CDCl_3$): δ 7.75-7.55 (bs, 2H, ortho CONH), 6.80-6.66 (bs, 2H, ortho NH_2), 4.30-3.70 (bs, 2H, NH_2), 1.80-1.20 (bm, H TEMPO). ^{13}C NMR ($CDCl_3$): δ 167.1, 149.9, 129.0, 114.5, 41.2, 31.1, 29.8, 22.8, 14.2. ESI-MS: calculated for $C_{22}H_{17}NO_4$ 290; found: +MS $[M+H]^+$ 291, $[M+Na]^+$ 313, $[2M+Na]^+$ 603; -MS $[M-H]^-$ 289, $[M+Cl]^-$ 325, $[2M+Cl]^-$ 615. IR (ATR) cm^{-1}: 3446, 3336, 3215, 2977, 2943, 1621, 1605, 1568, 1533, 1505, 1365, 1322, 1177, 848, 772. Mp = 213-215°C

RESULTS

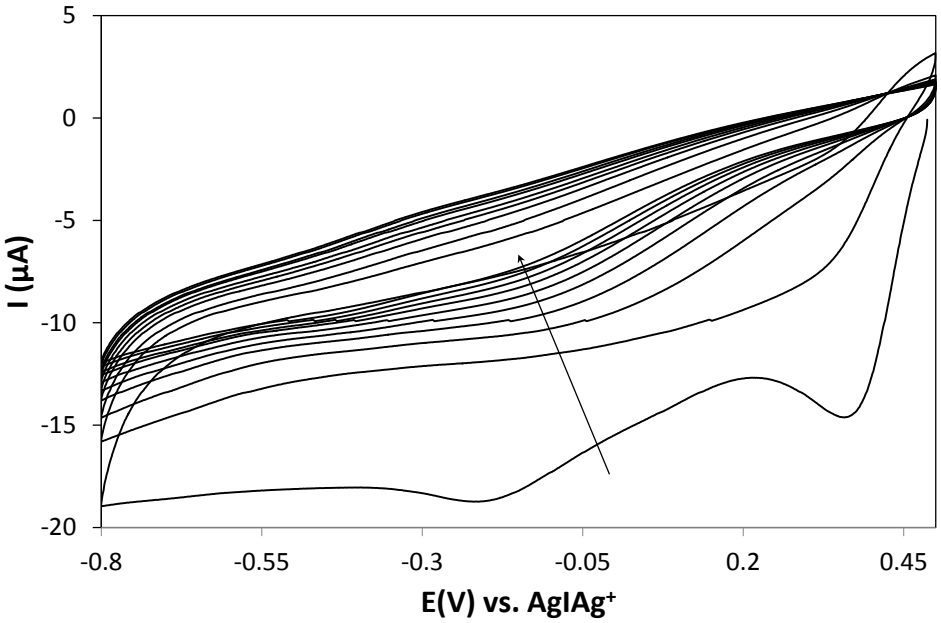


Figure S1: Repetitive cyclic voltamograms of a gold electrode recorded at 50 mV/s in HCl/acetonitrile mixture (4/96, v/v) containing 1 mM ABzTEMPO in presence of 3 equivalents of $NaNO_2$.

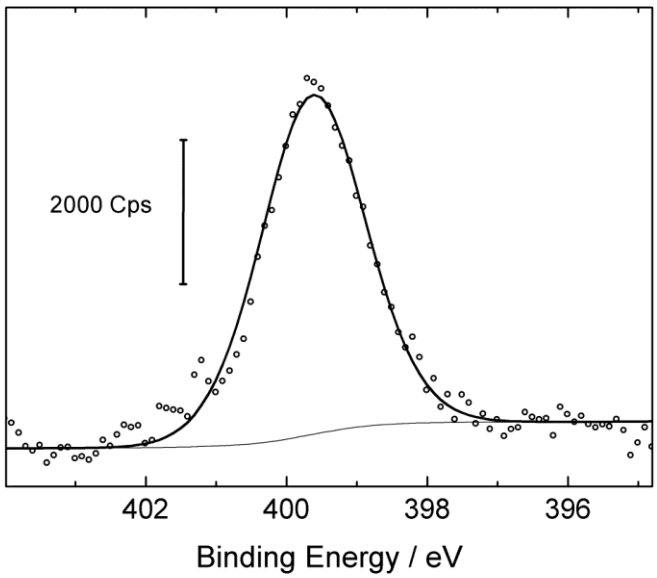


Figure S2: N_{1s} core level spectra for PVD gold surface modified by electroreduction of ABzTEMPO in protic media.

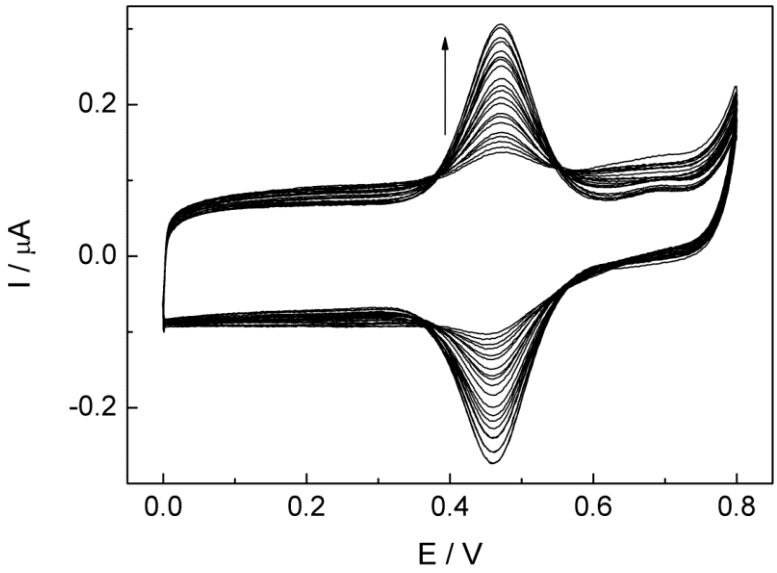


Figure S3: Repetitive CVs recorded in acetonitrile + 0.1 M Bu_4NPF_6 onto a modified gold electrode prepared by the route 2. Scan rate: 50 mVs^{-1}.