Supporting Information on

No more compromise: A facile route towards functionalized surfaces with stable monolayers

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Experimental procedures

Reagents. Tetrabutylammonium hexafluorophosphate (nBu_4NPF_6 – Sigma-Aldrich), dichloromethane (HPLC grade, Carlo Erba) and tert-butyl nitrite (tBuONO – Sigma-Aldrich) were used as received.

Synthesis. The synthesis of $AC_{12}Fc$ compound has already been described in the literature[1] and the synthesis of the AC_2Fc compound and its characterization are detailed below (part SI-2).

Surface modifications procedures. Home-made Au disk electrodes of 5 mm diameter were prepared by evaporation of ca. 5 nm of chromium followed by ca. 100 nm of gold onto glass slides, previously cleaned by sonication with water, acetone and ethanol and dried at 90 °C for 1 h.[2]

Diazonium salts were generated in-situ from a 10^{-3} M solution of the amine in CH_2Cl_2 by addition of 5 equivalents of tBuONO. The salt was then spontaneously reduced by immersing the gold electrodes in the solution for various times. Electrodes were rinsed and sonicated in CH_2Cl_2 for 1 min before analysis.

Electrochemistry. A BioLogic VSP potentiostat monitored by ECLab software was used for the electrochemical experiments. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum-plate counter electrode, an $Ag/AgNO_3$ (0.01 M CH_3CN) reference electrode and home-made PVD gold substrates as working electrodes. CVs were recorded in 0.1 M nBu_4NPF_6 in dry HPLC-grade dichloromethane.

AFM measurements. AFM studies were carried out with a NanoObserver Microscope from CSInstruments. The acquired images and 3D representations were processed with the Gwyddion free SPM data analysis software. Pyrolyzed Photoresist Film (PPF) electrodes were used to estimate the thickness of the deposited layers according to the "scratching" technique.[3] The thickness was calculated using a mathematical function (Edge height, Gwyddion) applied to this profile and error on the thickness is given by this adjustment. Probes: silicon probes purchased from AppNano.

XPS measurements. XPS data were collected using a Kratos Axis Ultra spectrometer. The X-ray source was monochromated Al Kα working at 1486.6 eV. Spectra were accumulated at a take-off angle of 90°, using a spot size of 0.7 × 0.3 mm^2 at a pressure of less than 10^{-8} mbar. High-resolution scans were carried out with a step size of 0.1 eV and a pass energy of 20 eV. All spectra were calibrated taking C1s as a reference binding energy of 284.5 eV, without an internal standard. XPS spectra were analyzed using the curve-fitting program CASA XPS and involved background subtraction using U 2 Tougaard and a subsequent pseudo-Voigt function mixing Gaussian–Lorentzian functions.

Synthesis and characterization of AC_2Fc compound

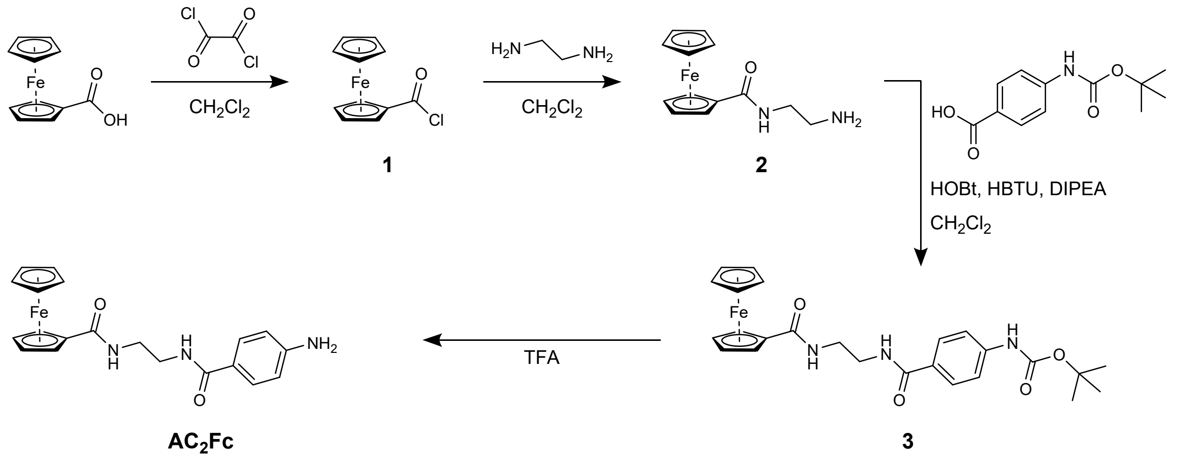

Figure SI-1. Synthesis of AC_2Fc.

Ferrocenecarbonyl chloride (1)

500 mg of ferrocenecarboxylic acid (2.17 mmol) were dissolved in 30 mL of CH_2Cl_2. 520 µL of oxalyl chloride (749 mg – 5.9 mmol – 2.7 eq) were added dropwise to the solution. The mixture was left under stirring for 2h at room temperature. After evaporation of the solvent, the reaction quantitatively yields to a dark orange solid.

NMR^{1}H (300 MHz, $CDCl_3$) δ = 4.34 ppm (s, 5H), 4.64 ppm (t, J = 1.8 Hz, 2H), 4.92 ppm (t, J = 1.5 Hz, 2H).

MS (EI): 248.00 ($M^{\bullet+}$), calculated for $C_{11}H_9ClFeO$: 247.97.

N-ferrocenecarbonyl-1,2-diaminoethane (2)

1.2 g of ethylene diamine (20.1 mmol – 10 eq) were dissolved in 20 mL of CH_2Cl_2. 500 mg of ferrocenecarbonyl chloride (2 mmol – 1 eq) were dissolved in 30 mL of CH_2Cl_2, this solution was added to the previous one, dropwise on 30 minutes. The mixture was left under stirring overnight at room temperature. The organic phase was washed twice by 80 mL of KOH 10% wt and dried over $MgSO_4$. The product was purified by silica-gel column chromatography with CH_2Cl_2/MeOH 9/1 to 8/2. The product was isolated as an orange solid with a 71% yield.

NMR^{1}H (300 MHz, $CDCl_3$) δ = 6.94 ppm (s, 2H), 4.76 ppm (s, 2H), 4.30 ppm (s, 2H), 4.18 ppm (s, 5H), 3.45 ppm (s, 4H), 2.93 ppm (s, 2H).

MS (EI): 272.13 ($M^{\bullet+}$), calculated for $C_{13}H_{16}FeN_2O$: 272.06.

N-Bocaminobenzoyl-N'-ferrocenecarbonyl-1,2-diaminoethane (3)

261.6 mg of Boc-4-Abz-OH (1.10 mmol – 1 eq), 149.0 mg of 1-hydroxybenzotriazole (1.10 mmol – 1 eq), 385 µL of N,N-diisopropylethylamine (2.20 mmol – 2 eq) and 354.0 mg de O-(Benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (1.10 mmol – 1 eq) were dissolved in 60 mL of CH_2Cl_2. 300 mg of N-ferrocenecarbonyl-1,2-diaminoethane were added after 1h of stirring at room temperature. The mixture was left under stirring for 48h. Organic phase was then washed with 3 times 80 mL of HCl 5% wt and dried over $MgSO_4$. 553 mg of an orange solid were then collected from evaporation of the organic phase with a 100% yield. Product was used without further purification. NMR^{1}H (300 MHz, $(CD_3)_2SO$) δ = 8.72 ppm (s, 1H), 6.88 ppm (d, J = 9 Hz, 2H), 6.62 ppm (d, J = 9 Hz, 2H), 3.87 ppm (t, J = 1.8 Hz, 2H), 3.44 ppm (t, J = 1.8 Hz, 2H), 3.22 ppm (s, 5H), 1.60 ppm (m, 4H), 0.58 ppm (s, 9H).

MS (EI): 491.22 ($M^{\bullet+}$), calculated for $C_{25}H_{29}FeN_3O_4$: 491.15.

N-(2-ferrocenamidoethyl)-4-aminobenzamide (AC$_2$Fc)

300 mg of N-Bocaminobenzoyl-N’-ferrocenecarbonyl-1,2-diaminoethane were placed in a flask and 5 mL of trifluoroacetic acid were then added dropwise at 0°C. The mixture was left under stirring for 30 min at room temperature. 100 mL of distillated water were then added to dilute the medium. Acid was neutralized using K_2CO_3. The product was extracted using $CHCl_3$ and the organic phase was dried over $MgSO_4$. Final purification was performed by silica gel chromatographic column using $CHCl_3$/MeOH 96/4 as eluent. 110 mg of an orange solid are collected with a 46% yield.

NMR^{1}H (300 MHz, CD_3OD) δ = 7.64 ppm (d, J = 8.7 Hz, 2H), 7.64 ppm (d, J = 8.7 Hz, 2H), 4.78 ppm (t, J = 2.1 Hz, 2H), 4.39 ppm (t, J = 2.1 Hz, 2H), 4.13 ppm (s, 5H), 3.54 ppm (m, 4H).

NMR^{13}C (300 MHz, CD_3OD) δ = 174.35 ppm, 170.93 ppm, 153.36 ppm, 130.05 ppm, 122.87 ppm, 114.77 ppm, 76.48 ppm, 71.83 ppm, 70.85 ppm, 69.41 ppm, 41.20 ppm, 40.82 ppm.

HRMS (MALDI-TOF, DCTB): 391.10 ($M^{\bullet+}$), calculated for $C_{20}H_{21}FeN_3O_2$: 391.10.

Comparative voltammetric study of bare Fc and $DC_{12}Fc$

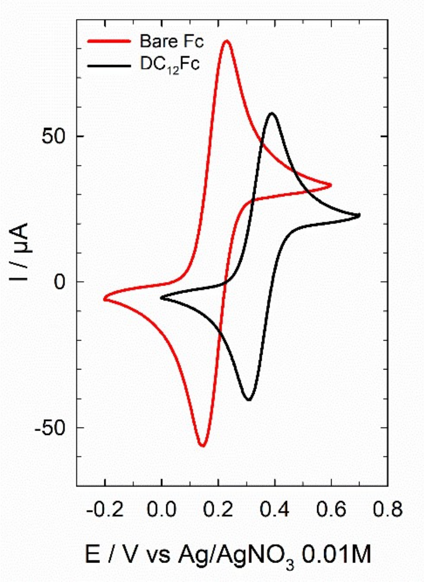

Figure SI-2. Cyclic voltammograms recorded in 0.1 M nBu_4NPF_6 *in dichloromethane containing 1 mM bare Fc (black line) or 1 mM* $DC_{12}Fc$ *(red line) on a gold working electrode (diameter: 0.5 cm). Scan rate: 100* $mV.s^{-1}$.

Multiple-scan rate CV experiments on $C_{12}Fc$ and C_2Fc layers

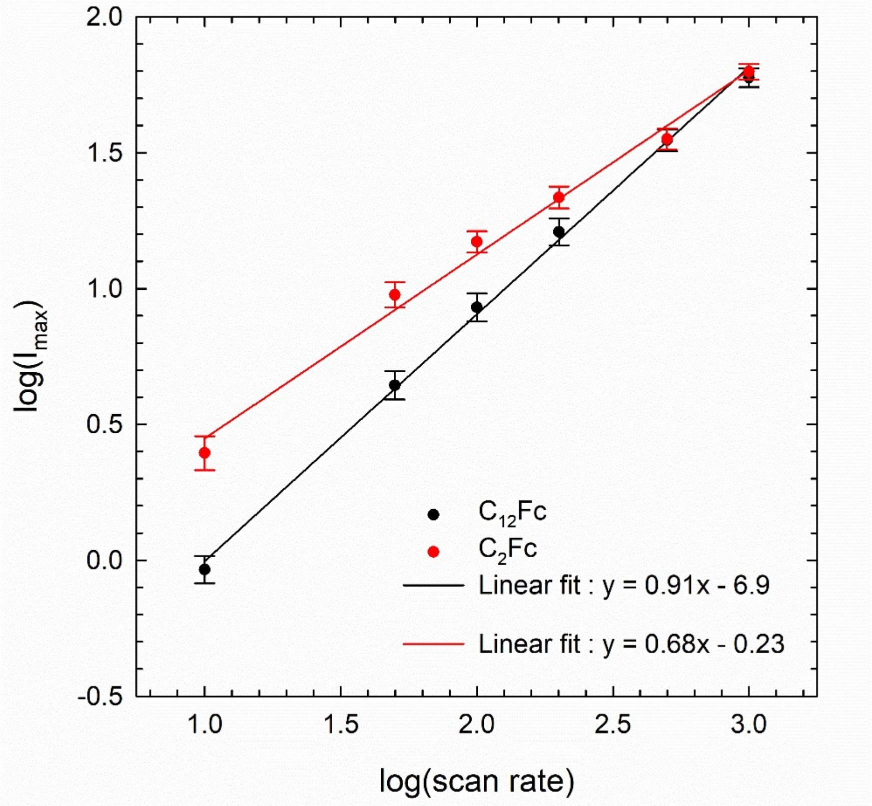

Figure SI-3. Log(peak current) vs. log(scan rate), obtained from cyclic voltammograms recorded in 0.1 M nBu_4NPF_6 *in dichloromethane on layers spontaneously prepared from* $DC_{12}Fc$ *(black line) or from* DC_2Fc *(red line), by 7 h-immersion in 1 mM aniline derivative + 5 mM tBuONO in dichloromethane.*

XPS Fe2p and Au4f core-level spectra

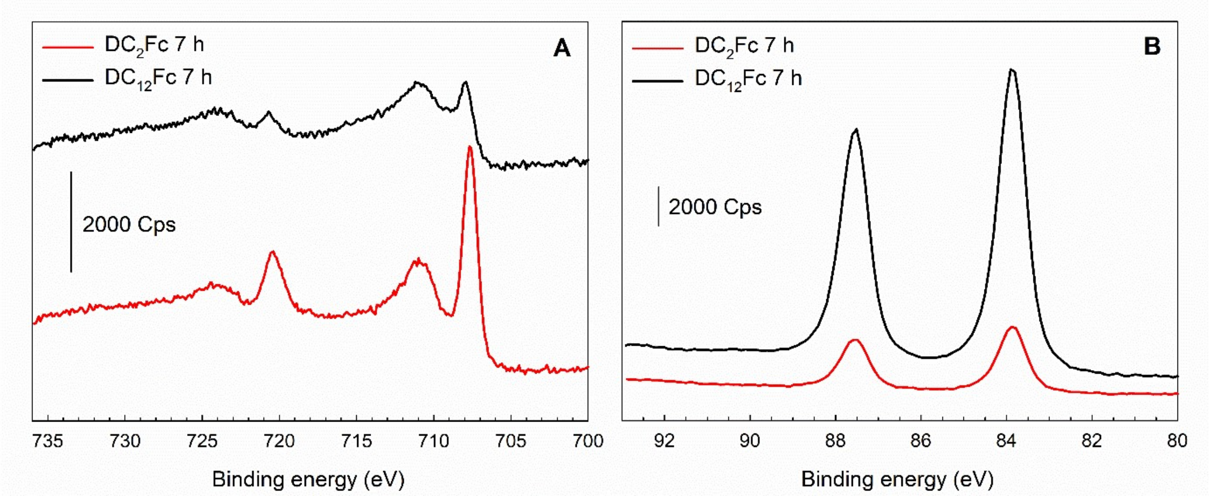

Figure SI-4. A. XPS Fe2p core-level spectra. B. XPS Au4f core-level spectra. Measurements were recorded on PVD gold substrates modified by 7 h-immersion in $DC_{12}Fc$ (formed in-situ from 1 mM $AC_{12}Fc$ + 5 mM tBuONO, black line) or in DC_2Fc (formed in-situ from 1 mM AC_2Fc + 5 mM tBuONO, red line) in dichloromethane.

AFM analyses of C_2Fc layers

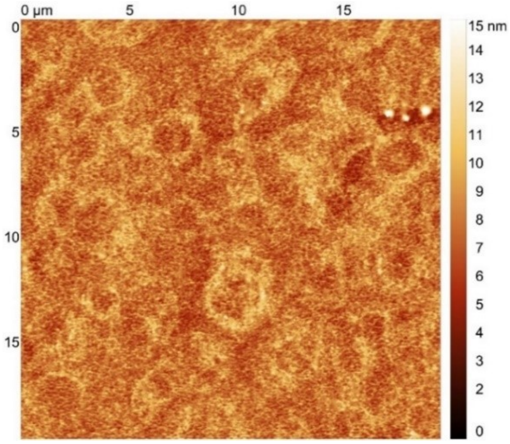

Figure SI-5. AFM Image of a C_2Fc layer obtained by a 9 h-immersion of a PPF substrate (RMS≈2 nm).

References

(1) Tanaka, M.; Sawaguchi, T.; Sato, Y.; Yoshioka, K.; Niwa, O. Surface Modification of GC and HOPG with Diazonium, Amine, Azide, and Olefin Derivatives. *Langmuir* **2011**, *27* (1), 170–178. https://doi.org/10.1021/la1035757.

(2) Alévêque, O.; Blanchard, P.-Y.; Breton, T.; Dias, M.; Gautier, C.; Levillain, E. Revisiting the Determination of Full Steady-State Coverage of Redox Centers on Self-Assembled Monolayers. *Electrochem. Commun.* **2012**, *16* (1), 6–9. https://doi.org/10.1016/j.elecom.2011.12.014.

(3) Brooksby, P. A.; Downard, A. J. Electrochemical and Atomic Force Microscopy Study of Carbon Surface Modification via Diazonium Reduction in Aqueous and Acetonitrile Solutions. *Langmuir* **2004**, *20* (12), 5038–5045. https://doi.org/10.1021/la049616i.