

Tetraferrocenylporphyrins as active components of self-assembled monolayers on gold surface

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Supporting Information

Experimental section

Synthesis of 5,10,15,20-tetraferrocenylporphyrin (H₂TFcP)

1.2 g of ferrocenecarboxaldehyde (FcCHO, 5,6 mmol) were dissolved in 150 ml of anhydrous CH₂Cl₂. To this solution, 1.1 equivalents of pyrrole (6 mmol, 413 μl) and 5 % of BF₃·Et₂O (0.3 mmol) as catalyst were added. All additions were carried out under a nitrogen stream. The reaction mixture was kept in the dark and under nitrogen atmosphere for 20 hours. After this period, 980 mg of *p*-chloranil (4 mmol) were added and the mixture was refluxed for an hour. The solution was cooled down, concentrated and filtered over neutral and Al₂O₃ deactivated with 5% of water. The solvent was then evaporated and the solid was dissolved in the minimum volume of toluene and precipitated with hexane. The solution was filtered through a medium frit and rinsed with hexane.

470 mg of a fine, dark green powder were obtained for a 32% yield.

¹HNMR (CDCl₃): δ (ppm) 9.64 (s, 8H, β-pyrrole), 5.34 (t, 8H, α in substitute Cp), 4,83 (t, 8H, β in substitute Cp) 4.00 (s, 20H, Cp), -0.46 (br s, 2H, internal NH).

Synthesis of Zinc 5,10,15,20-tetraferrocenylporphyrin (ZnTFcP) 110 mg of H₂TFcP (0.105 mmol) were dissolved in 10 ml of of anhydrous CH₂Cl₂ and a saturated solution of Zn(OAc)₂ in MeOH (0.5 g in 3 ml) was added. After one hour at room temperature the conversion was complete and the reaction mixture was diluted with CH₂Cl₂ and extracted with water. The organic layer is dried over Na₂SO₄, filtered, concentrated and purified over a plug of neutral and Al₂O₃ deactivated with 5% of water. The solvent was removed and the solid is precipitated with toluene/hexane to obtain 85 mg of a fine, green-brown powder for a 73% yield.

¹HNMR (CDCl₃): δ (ppm) 9.88 (s, 8H, β-pyrrole), 5.42 (t, 8H, α in substitute Cp), 4,81 (t, 8H, β in substitute Cp) 4.05 (s, 20H, Cp).

Synthesis of 1'-(6-bromohexanoyl)ferrocencarboxaldehyde

Aluminum Chloride (1.12 g, 1.2 equivalents) was slowly added to a solution of FcCHO (1.5 g, 7 mmol) in 45 ml of anhydrous CH₂Cl₂ under a nitrogen stream. In another round flask, 2 equivalents of 6-bromohexanoyl chloride were dissolved in 55 ml of anhydrous CH₂Cl₂ under a nitrogen stream. To this solution, 2.4 equivalents of AlCl₃ were slowly added. The solution containing the acyl chloride was then dropwise added to that containing FcCHO, in 20 minutes at 0°C. After this period, the reaction mixture was kept at room temperature and under a nitrogen atmosphere for 5 hours. The reaction was then quenched by the addition of about 100 g of ice and extracted. The crude product was chromatographed on silica gel using an hexane-AcOEt (3:2 v/v) mixture as the eluent. The red solid was rinsed with pentane to obtain 1.80 g of the pure product (66% yield).

¹HNMR (CDCl₃): δ (ppm) 10.07 (s, 1H, CHO), 4.99 (t, 2H, CH α), 4.92 (t, 2H, CH α'), 4.73 (t, 2H, CH β'), 4.69 (t, 2H, CH β), 3.58 (t, 2H, CH₂Br), 2.80 (t, 2H, CH₂CO), 2.06 (m, 2H, C(4)H₂), 1.88 (m, 2H, C(2)H₂), 1.69 (m, 2H, C(3)H₂).

¹³CNMR (CDCl₃): δ (ppm) 192 (CHO), 71 (CH α), 70 (CH α'), 73 (CH β'), 74 (CH β), 34 (CH₂Br), 39 (CH₂CO), 33 (C(4)H₂), 28 (C(3)H₂), 23 (C(2)H₂).

Synthesis of 5-[1'-(6-bromohexanoyl)]ferrocenyl-10,15,20-triferrocenylporphyrin A mixture of 1'-(6-bromohexanoyl)-ferrocencarboxaldehyde (250 mg, 0.64 mmol) and 5 equivalents of FcCHO (684 mg, 3.2 mmol) were dissolved in 100 ml of anhydrous CH₂Cl₂. To this solution 6 equivalents of pyrrole (266 μl) and 0.1 equivalents of BF₃·Et₂O were added (40 μl). All additions were performed under a nitrogen stream. The reaction mixture was kept under nitrogen atmosphere, at room temperature and in the dark for 4 hours. After this period, 600 mg of *p*-chloranil (4 equivalents) were added and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was purified by column chromatography on 10% deactivated Al₂O₃ using the mixture hexane-CH₂Cl₂ 1:1 v/v as the eluent. H₂TFcP (115 mg, 14.4% yield) was recovered as the first band and traces of FcCHO unreacted was also recovered. The third compound isolated was the desired monosubstituted porphyrin (70 mg, 9% yield).

¹HNMR (CDCl₃): δ (ppm) 9.64 (s, 4H, H β-pyrrolic), 9.67 (d, 2H, H β-pyrrolic), 9.54 (d, 2H, H β-pyrrolic), 5.39 (t, 2H, CH α'), 5.36 (t, 8H, CH α), 4.80 (t, 8H, CH β), 4.78 (t, 2H, CH β'), 4.02 (s, 5H, Cp *trans*) 4.00 (s, 10 H, Cp *cis*), 3.27 (t, 2H, CH₂Br), 2.54 (t, 2H, CH₂CO), -0.5 (s, 2H, internal NH).

MS (FAB- 3-nitrobenzyl alcohol): *m/z* 1225 (M+H⁺)

Synthesis of 5-[1'-(6-thioacetylhexanoyl)]ferrocenyl-10,15,20-triferrocenylporphyrin 22 mg of 5-[1'-(6-bromohexanoyl)]ferrocenyl-10,15,20-triferrocenylporphyrin (0.018 mmol) were dissolved in 2 ml of dry DMF and 3 equivalents of potassium thioacetate were added. The solution was kept at room temperature and under nitrogen atmosphere for 18 hours. The reaction mixture was then diluted with 30 ml of EtOAc and rinsed ten times with 40 ml of water each time. The reaction mixture was dried on Na₂SO₄ and the solvent removed under reduced pressure. The crude product was chromatographed on Al₂O₃ deactivated with 5% of water using the mixture hexane-CHCl₃ 1:1 v/v to afford a green solid, that was dissolved in the minimum volume of toluene and precipitated with hexane. The solution was decanted and 13 mg of a green powder were recovered (60% yield).

¹HNMR (CDCl₃): δ (ppm) 9.65 (s, 4H, H β-pyrrolic), 9.67 (d, 2H, H β-pyrrolic), 9.55 (d, 2H, H β-pyrrolic), 5.39 (t, 2H, CH α'), 5.36 (t, 8H, CH α), 4.80 (t, 8H, CH β), 4.78 (t, 2H, CH β'), 4.01 (s, 5H, Cp *trans*) 4.00 (s, 10 H, Cp *cis*), 2.67 (t, 2H, CH₂SCO), 2.44 (t, 2H, CH₂CO), 2.35 (s, 3H, SCOCH₃), -0.5 (s, 2H, internal NH).

MS (FAB- 3-nitrobenzyl alcohol): *m/z* 1220 (M+H⁺)

Synthesis of 11-(*N*-imidazolyl)-1-undecanol Imidazole (554 mg, 8 mmol) was dissolved in 20 ml of dry THF and 300 mg (8.8 mmol) of a suspension of 80% NaH was slowly added under a nitrogen stream. The solution was stirred at room temperature and under nitrogen atmosphere for 30 minutes. After this period a solution of 1 g (4 mmol) of 11-bromo-1-undecanol in 20 ml of dry THF was added dropwise. An abundant, white precipitate was formed during the reaction. After 24 hours the solvent was evaporated, the white solid was dissolved in the minimum volume of MeOH and purified on a silica gel column, using the mixture CHCl₃-MeOH 95:5 v/v as the eluent. A pale-yellow oil was obtained, that was precipitated with hexane to afford 870 mg of a white solid for a 91% yield.

¹HNMR (CDCl₃): δ (ppm) 7.50 (s, 1H, a), 7.06 (s, 1H, b), 6.91 (s, 1H, c), 3.94 (t, 2H, CH₂Im), 3.66 (t, 2H, CH₂OH), 2.44 (s, 1H, OH), 1.78 (m, 2H, d), 1.57 (m, 2H, e), 1.27 (m, 14H, -CH₂-).

Synthesis of 11-(*N*-imidazolyl)-1-undecyl thioacetate 206 mg of 11-(*N*-imidazolyl)-1-undecanol (0.86 mmol) were dissolved in 3 ml of CHCl₃ previously filtered over basic alumina. To this solution 140 μl of pyridine and, slowly and at 0°C, 247 mg of tosyl chloride (1.5 equivalents) were added. The reaction mixture was left at 0°C and under nitrogen atmosphere for 75 minutes. After this period the solvent was removed under reduced pressure and the crude product was dissolved in 5 ml of anhydrous acetone. 198 mg of potassium thioacetate were added under anhydrous

conditions and the mixture was left for 18 hours at room temperature and under nitrogen atmosphere. The reaction mixture was diluted with 30 ml of CH₂Cl₂, extracted with a solution of a 10% aqueous NH₄Cl and washed thrice with water. The crude product was then chromatographed on silica gel using the mixture EtOAc-MeOH 95:5 v/v as the eluent. The purification afforded 226 mg (88% yield) of an orange solid that was crystallized with pentane to obtain tiny ivory needles. ¹HNMR (CDCl₃): δ (ppm) 7.69 (s, 1H, a) 7.14 (s, 1H, b), 6.97 (s, 1H, c), 3.98 (t, 2H, CH₂Im), 2.87 (t, 2H, CH₂SCO), 2.34 (s, 3H, SCOCH₃), 1.80 (m, 2H, d), 1.57 (m, 2H, e), 1.27 (m, 14H, -CH₂).

Preparation and characterization of SAMs

Self-Assembled Monolayers (SAMs) were prepared onto two different gold-containing media. A glass with a 5 nm gold layer was used for the UV-Vis characterization, while a gold foil (1 x 0.5 cm) was used as the working electrode for electrochemistry and photocurrent generation experiments. Before the functionalization, the gold foils were immersed for 15 minutes in a "piranha solution" (H₂SO₄-H₂O₂ 1:1 v/v), while 10 seconds were enough to clean the glass. Both the media were thoroughly rinsed with distilled water and then with CH₂Cl₂. SAM **1** was prepared by soaking a clean gold foil in a 1 mM solution of the porphyrin for 20 hours in CH₂Cl₂. As to the mixed SAM **2**, the coating solution was prepared at a 5:1 ratio of the ligands with a concentration of 1 mM of the alkanethiols and 0.2 mM of the porphyrin in CH₂Cl₂. SAM **3** was prepared by dipping the gold containing medium in a 1 mM solution of 11-(*N*-imidazolyl)-1-undecyl thioacetate for 20 hours in CH₂Cl₂. The monolayer was rinsed many times with CH₂Cl₂ and then immersed in a 1 mM solution of ZnTFcP in CH₂Cl₂ for 30 minutes. SAM **4** was obtained by a 1 mM of octanethiole and 0.2 mM of 11-(*N*-imidazolyl)-1-undecyl thioacetate coating solution. The coordinative step was the same used for SAM **3**. All the obtained monolayers were then rinsed many times with CH₂Cl₂ and dried under nitrogen stream.

The formation of the film was monitored by cyclic voltammetry with a redox-active probe such as K₃[Fe(CN)₆]. With unfuctionalized gold foil, the probe can reach the electrode and an intense, reversible signal is observed, while when the SAM is densely packed the electrode is passivated and the signal disappears (see figure S1).

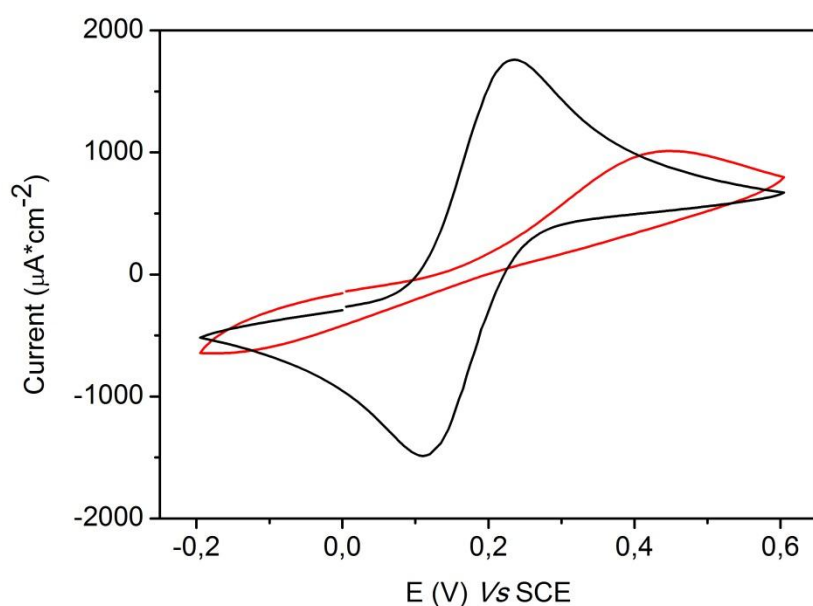


Fig. S1 CV of $K_3[Fe(CN)_6]$ 50 mM in water using as working electrode a clean gold foil (black line) and the densely packed SAM **2** on a gold foil (red line). The curves are corrected for the immersed area.

Quantitative data on the density of the porphyrin film was given by the CV on the modified electrode. These experiments were carried out in a 0.1 M solution of TBAP (tetrabutylammonium perchlorate) in acetonitrile. The integration of the oxidative peak on the graph gives the density of the redox-active molecules (Γ) on the electrode through the simple formula:¹

$$\Gamma = \frac{Q}{nFA}$$

Where Q is the quantity of charge in Coulomb calculated by the integral, n is the number of the electrons exchanged during the redox process ($n = 4$ for tetraferrocenylporphyrins), F is the Faraday constant ($F = 96485 \text{ C}\cdot\text{mol}^{-1}$) and A is the immersed area of the electrode that is calculated twice since both the faces of the electrode contribute to the signal. The quantity of charge Q was obtained by the sum:

$$Q = \Delta x \sum y_i$$

where y_i are the intensities in Ampere and Δx is the fixed difference in Volts between two experimental points (50 mV).

An important evidence of the “3+1” mechanism was provided by the calculation of the quantity of charge associated to the area delimited by the straight lines (figure S2). The integration of the area delimited by the green line yielded the global charge of the processes (4.008×10^{-5}) C. The individual integration of the areas yielded respectively (3.000 and 1.008) $\times 10^{-5}$ C thus indicating that the charge exchanged during the first process is three times bigger than that exchanged during the second one.

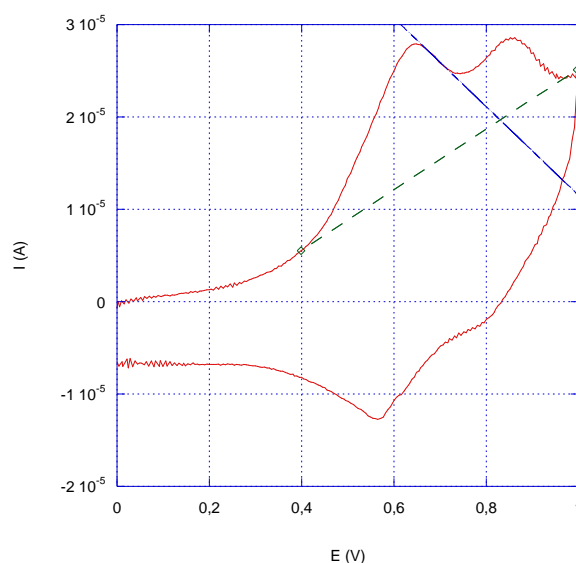


Fig. S2 CV in MeCN/TBAP 0.1 M of SAM 2 on a gold foil. The green, dashed line delimits the area associated to the whole charge exchanged during the two processes, while the blue line divides the area into 3 electrons process (first peak) and 1 electron process (second peak).

For SAMs **1** and **2** the Γ values were calculated both considering only the first process ($n=3$ in the equation) and the whole processes ($n=4$) obtaining comparable values. The reported Γ were calculated taking into account only the first peak, i.e. using $n=3$.

Photocurrent generation experiments

Photocurrent experiments were carried out in a (2x1) cm cuvette using a 50 mM solution of triethanolamine (TEOA) and 0.1 M of Na_2SO_4 in bidistilled water. An Ag/AgCl electrode was used as the reference and a Pt wire as counter electrode. The modified gold foil was employed as the working electrode. The measurements were carried out at a fixed applied potential (0.0 V) and by irradiating the photoelectrochemical cell at a given wavelength and alternating irradiation with 30 seconds of dark. The irradiation range was 300-800 nm and the experimental points were collected

every ten nm. The action spectrum is obtained by reporting the photocurrent intensity vs the excitation wavelength. The photocurrent intensity is calculated as the difference between the intensity of the irradiation and the dark phases.

PG experiments were also carried out without TEOA in an oxygen-saturated solution. O₂ was bubbled directly inside the cuvette for 15 minutes. An oxygen stream was kept on the top of the photoelectrochemical cell during the whole experiment. The same solution was then saturated with N₂ using the same procedure described above. Also in this case a nitrogen atmosphere was maintained during the acquisition. Although it was not possible to remove O₂ completely, a significant decrease in the photocurrent generation efficiency was observed (figure S3).

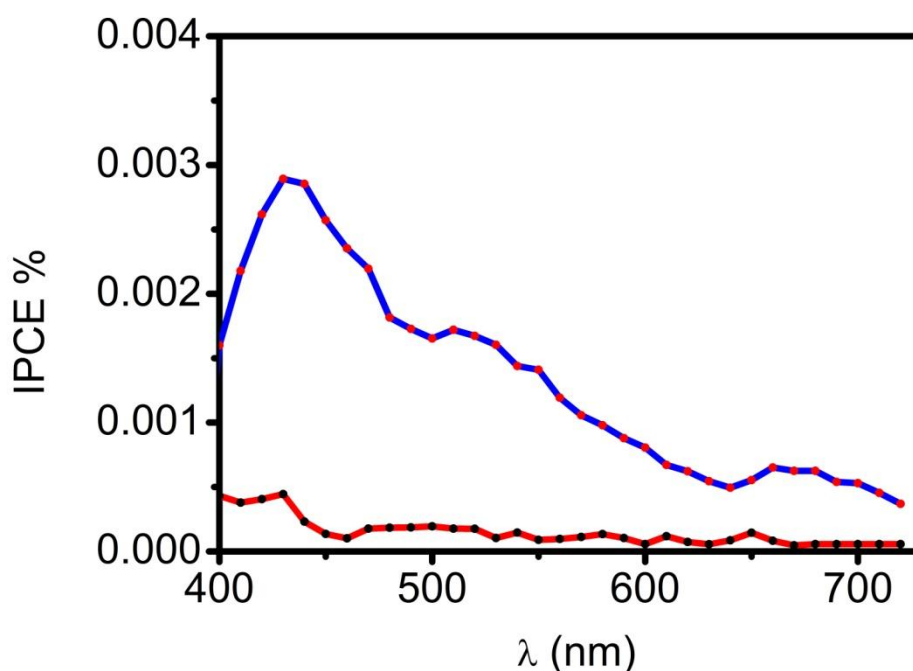


Fig. S3 Overlay of the IPCE spectra collected in a 0.1 M Na₂SO₄ aqueous solution saturated with O₂ (blue line with red circles) and N₂ (red line with black circles).

The Incident Photon-to-Current Efficiency (IPCE) was calculated from the photocurrent action spectra by the following equation:²

$$IPCE \% = \frac{100 \times i (A \times cm^{-2}) \times 1240}{I (W \times cm^{-2}) \times \lambda (nm)}$$

Where *i* is the measured current density, *I* is the incident light power density measured at each incident wavelength (λ).

References

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