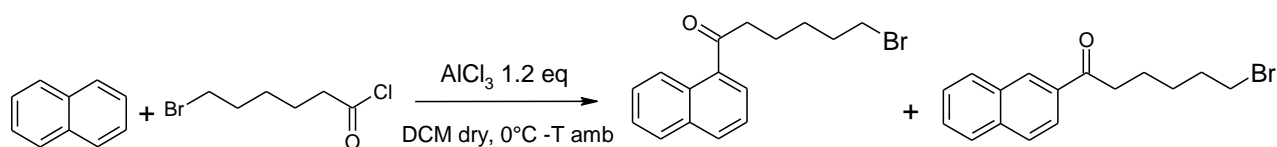


π -Interactions as a tool for an easy deposition of *meso*-tetraferrocenylporphyrin on surface

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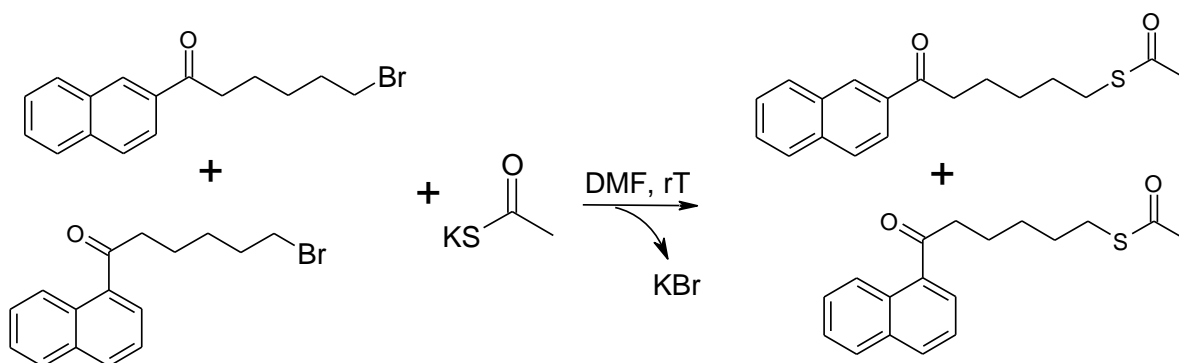
Supporting Informations

Synthesis of 1- and 2-(6-bromohexanoyl)naphthalene



506 mg of naphthalene (3,9 mmol) and 583 μl of 6-bromohexanoyl chloride (3,9 mmol) were dissolved in 10 ml of dry CH_2Cl_2 under a nitrogen stream. The solution was cooled down to 0°C with an ice bath and 1.2 equivalents of AlCl_3 (610 mg) were slowly added. The reaction mixture was stirred overnight at room temperature and under a nitrogen atmosphere. The solution was then diluted with 20 ml of CH_2Cl_2 and the reaction was quenched by the addition of about 100 g of ice. After the classical work-up the organic layer was dried under reduced pressure to obtain 1.109 g of the α and β isomers mixture for an overall 92% conversion.

Synthesis of 1- and 2-(6-acetylthiohexanoyl)naphthalene



The isomers mixture described above was reacted without purification. 982 mg of 6-bromohexanoylnaphthalene (3.3 mmol) were dissolved in 10 ml of dry DMF and 555 mg (1.5 equivalents) of potassium thioacetate were added. The solution was kept at room temperature and under a nitrogen atmosphere for 48 hours. The reaction mixture was then diluted with 50 ml of diethyl ether and rinsed several times with 50 ml aliquots of water each time. The reaction mixture was dried over Na_2SO_4 and the solvent removed under reduced pressure, to yield 970 mg of the isomers mixture for a quantitative conversion.

The crude product was chromatographed over silica gel using CH_2Cl_2 as eluent. Three fractions were collected: the α isomer was recovered first, and, after a mixed fraction, the β isomer was also isolated. Both compounds were crystallized with pentane to afford 169 mg of pure α -(6-acetylthiohexanoyl)naphthalene (17% yield) and 226 mg of pure β -(6-acetylthiohexanoyl)naphthalene (23% yield).

^1H NMR (α isomer, CDCl_3): δ (ppm) 8.56 (d, 1H, a), 8.00 (d, 1H), 7.87 (m, 2H), 7.56 (m, 3H), 3.08 (t, 2H, c), 2.90 (t, 2H, b), 2.34 (s, 3H, S- CH_3), 1.83 (m, 2H, $-\text{CH}_2-$), 1.66 (m, 2H, $-\text{CH}_2-$), 1.51 (m, 2H, $-\text{CH}_2-$). Elemental analysis: calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}$: C, 71.96; H, 6.71; S, 10.67; found: C, 73.01; H, 7.00; S, 8.89.

^1H NMR (β isomer, CDCl_3): δ (ppm) 8.48 (d, 1H, a), 8.01 (m, 2H), 7.89 (m, 2H), 7.59 (m, 3H), 3.12 (t, 2H, c), 2.91 (t, 2H, b), 2.34 (s, 3H, S- CH_3), 1.83 (m, 2H, $-\text{CH}_2-$), 1.67 (m, 2H, $-\text{CH}_2-$), 1.51 (m, 2H, $-\text{CH}_2-$). Elemental analysis: calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}$: C, 71.96; H, 6.71; S, 10.67; found: C, 72.21; H, 6.74; S, 9.29.

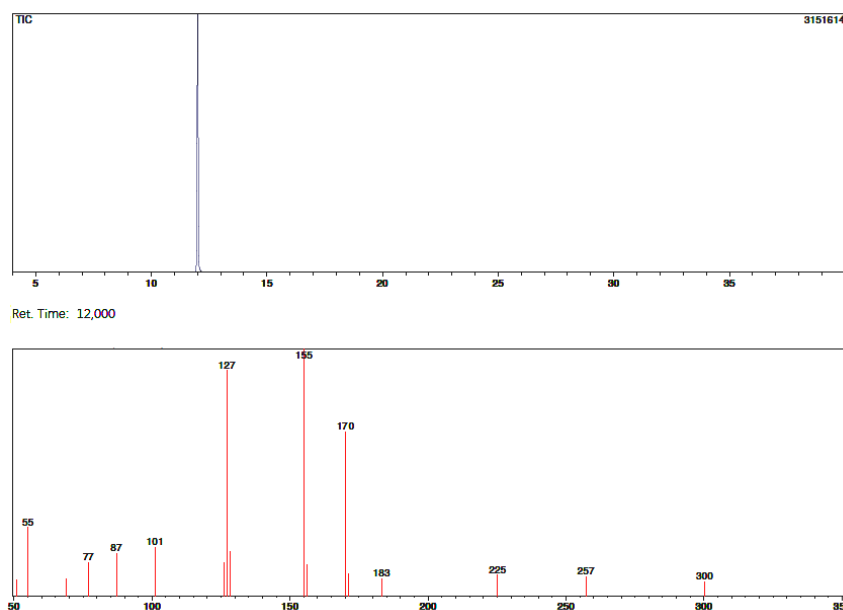


Fig. S1 Gas chromatogram (top) and mass spectrum (bottom) of 1-(6-acetylthiohexanoyl)naphthalene.

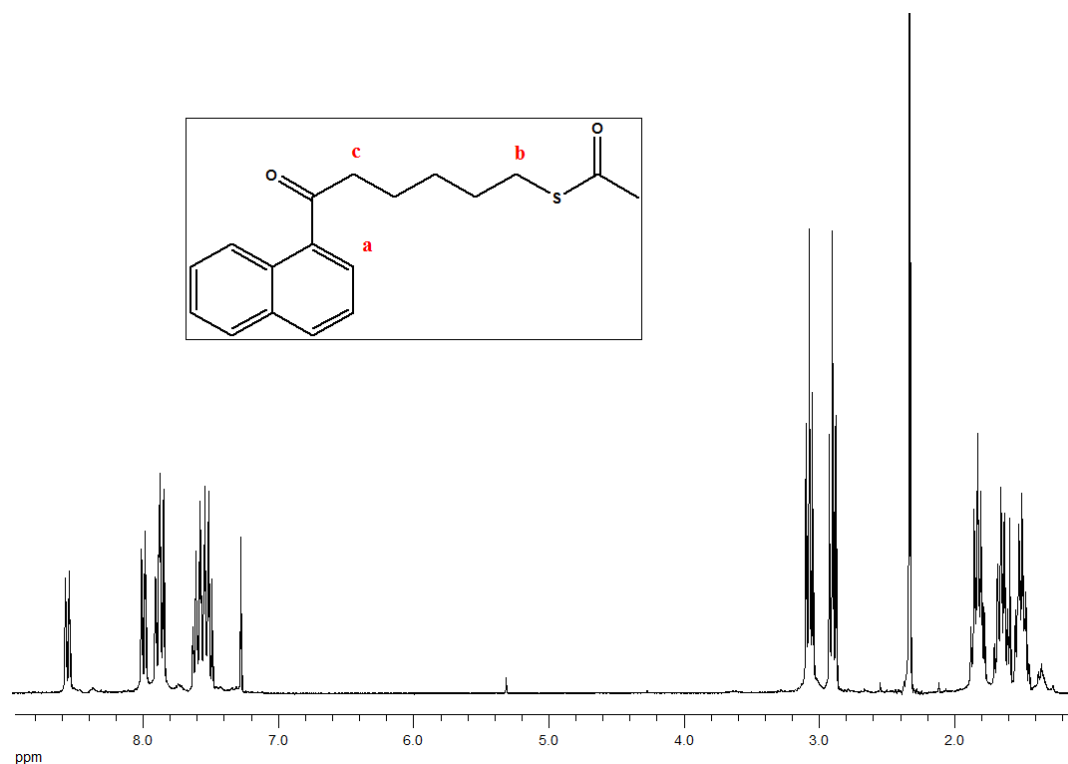


Fig. S2 ^1H NMR of α -(6-acetylthiohexanoyl)naphthalene in CDCl_3 . The structure is reported in the inset.

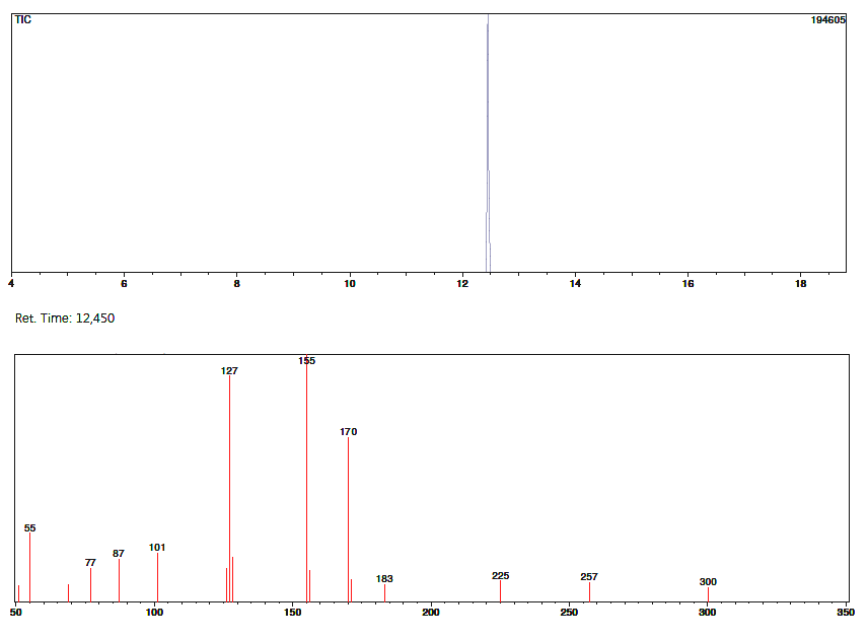


Fig. S3 Gas chromatogram (top) and mass spectrum (bottom) of 2-(6-acetylthiohexanoyl)naphthalene

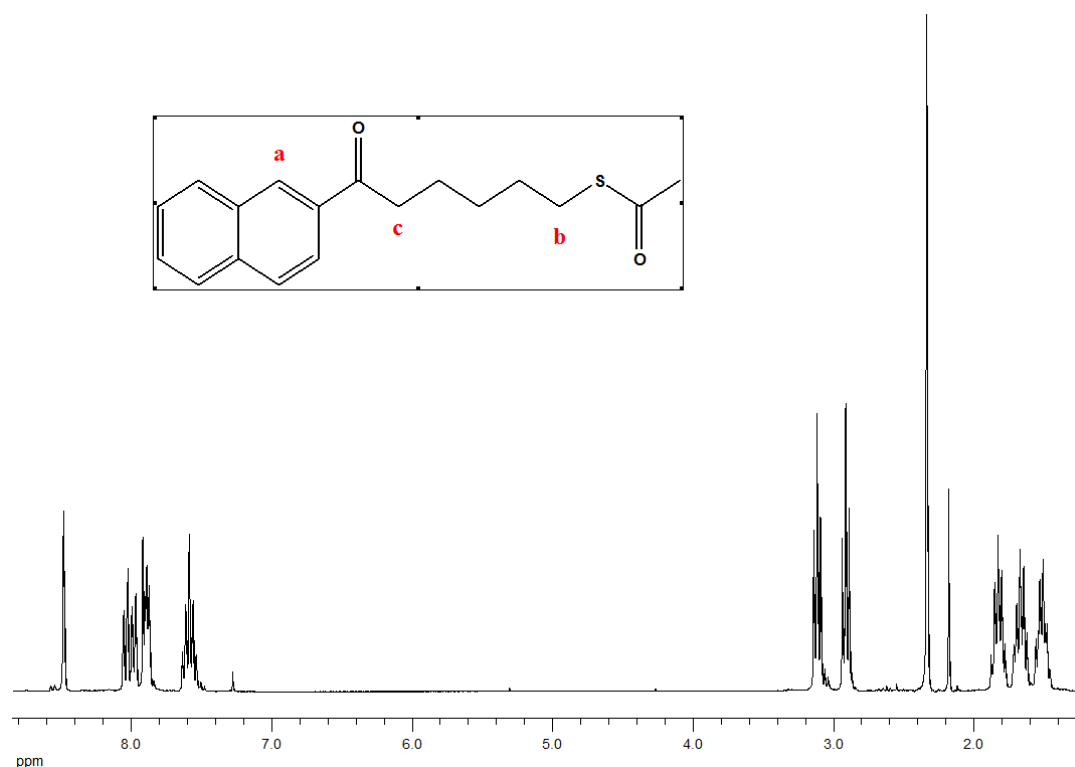
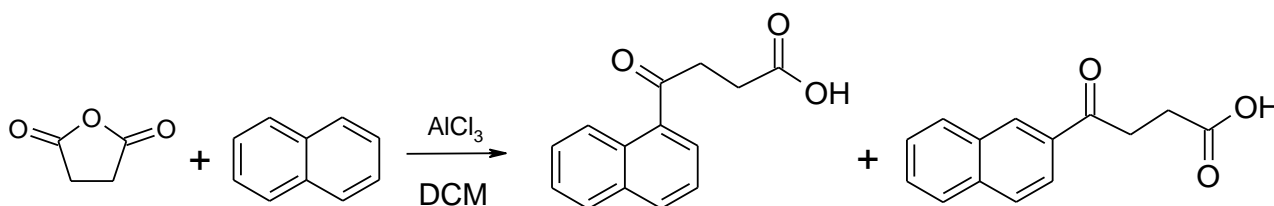


Fig. S4 ^1H NMR of 2-(6-acetylthiolhexanoyl)naphthalene in CDCl_3 . The structure is reported in the inset.

Synthesis of 4-naphthyl-4-oxobutanoic acid



Aluminium chloride (2.12 g, 15.9 mmol) was slowly added to a solution of succinic anhydride (778 mg, 7.8 mmol) in 15 ml of anhydrous CH_2Cl_2 under a nitrogen stream. To this mixture, a solution of naphthalene (986 mg, 7.7 mmol) in 5 ml of CH_2Cl_2 was added dropwise. The reaction mixture was kept at room temperature and under a nitrogen atmosphere for 24 hours. After this period the reaction was quenched by the addition of about 100 g of ice, extracted with 50 ml of a 10% solution of NH_4Cl and washed twice with 50 ml of water. The organic layer was then dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was chromatographed on silica gel using a CH_2Cl_2 /diethyl ether 1:2 v/v mixture as eluent. Unfortunately, such a purification did not

allow to isolate the isomers. The desired compounds were recovered as 762 mg of a mixture for an overall conversion of 43%.

Synthesis of ethyl 4-naphthyl-4-oxobutanoate

192 mg of 4-naphthyl-4-oxobutanoic acids (α + β mixture, 0.84 mmol) were dissolved in 11 ml of ethanol to which about 500 μ l of aqueous HCl were added dropwise. The reaction mixture was stirred at 40°C for 72 hours. After this period the ethanol solution was diluted with 50 ml of water and extracted trice with 20 ml of fresh CH₂Cl₂. The organic layer was then washed twice with 50 ml of water, dried over Na₂SO₄ and the solvent was removed under reduced pressure to afford 186 mg of α and β isomers for an overall 86% conversion.

The isomeric mixture was purified by column chromatography over SiO₂ using CH₂Cl₂ as eluent. Three fractions were collected: the α isomer was recovered first (85 mg, 40% yield), and, after a mixed fraction, the β isomer was also isolated (33 mg, 15% yield).

¹H NMR (α isomer, CDCl₃): δ (ppm) 8.61 (d, 1H, a), 7.97 (m, 2H), 7.89 (d, 1H), 7.55 (m, 3H), 4.20 (q, 2H, d), 3.39 (t, 2H, b), 2.85 (t, 2H, b), 1.30 (t, 3H, e). Elemental analysis: calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29; found: C, 76.31; H, 7.06.

¹H NMR (β isomer, CDCl₃): δ (ppm) 8.54 (s, 1H, a), 8.07 (d, 1H), 7.99 (d, 1H), 7.91 (m, 2H), 7.60 (m, 2H), 4.20 (q, 2H, d), 3.48 (t, 2H, b), 2.84 (t, 2H, b), 1.30 (t, 3H, e). Elemental analysis: calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29; found: C, 75.12; H, 6.88.

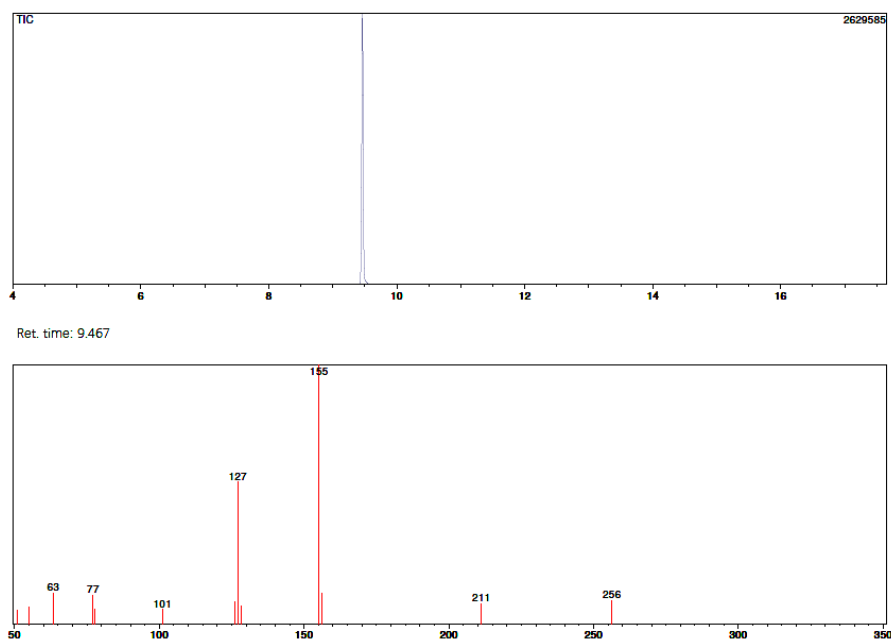


Fig. S5 Gas chromatogram (top) and mass spectrum (bottom) of ethyl 4-(1-naphthyl)-4-oxobutanoate

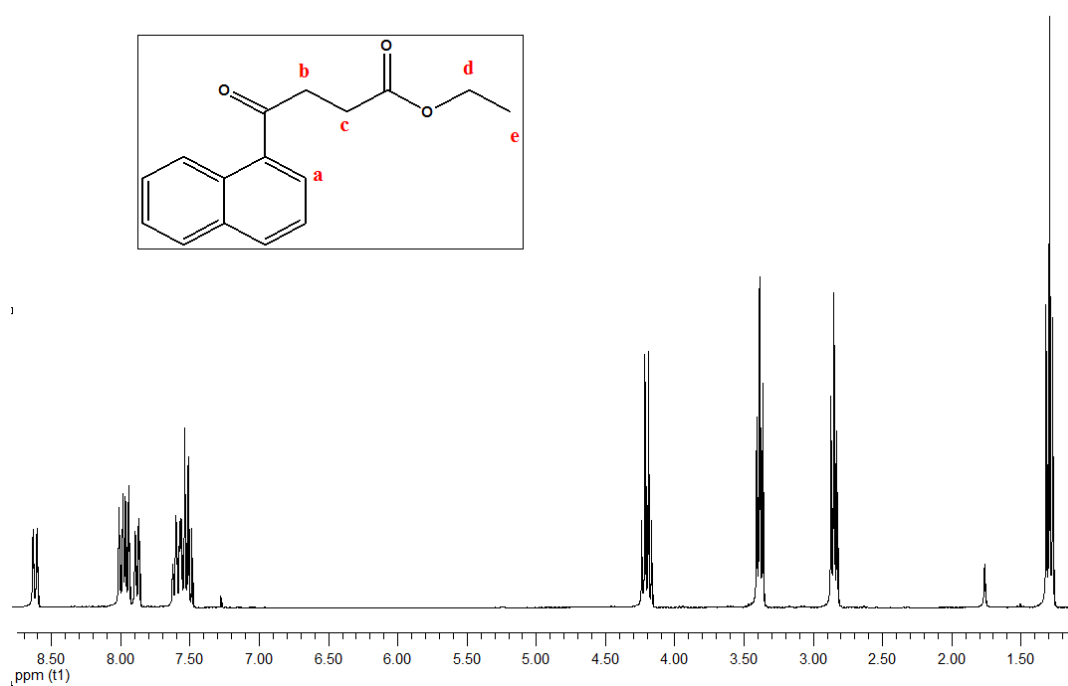


Fig. S6 ¹H NMR of ethyl 4-(1-naphthyl)-4-oxobutanoate in CDCl₃. The structure is reported in the inset.

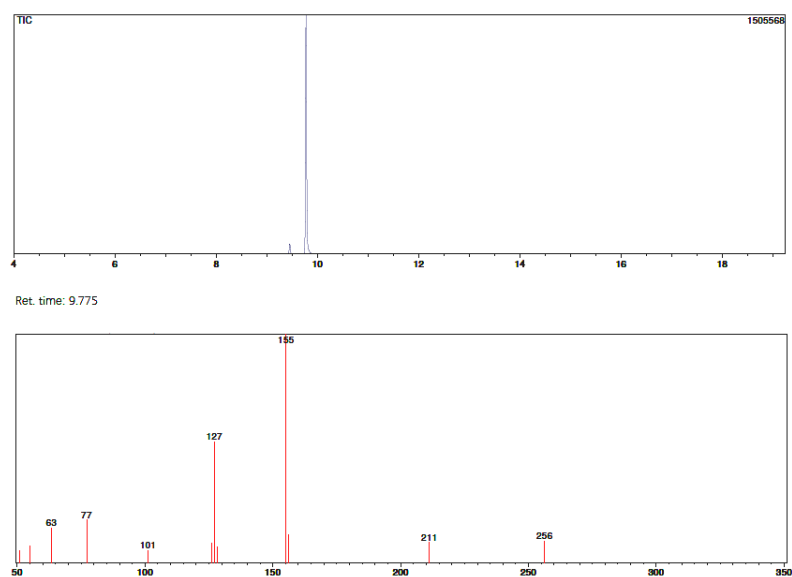


Fig. S7 Gas chromatogram (top) and mass spectrum (bottom) of ethyl 4-(2-naphthyl)-4-oxobutanoate

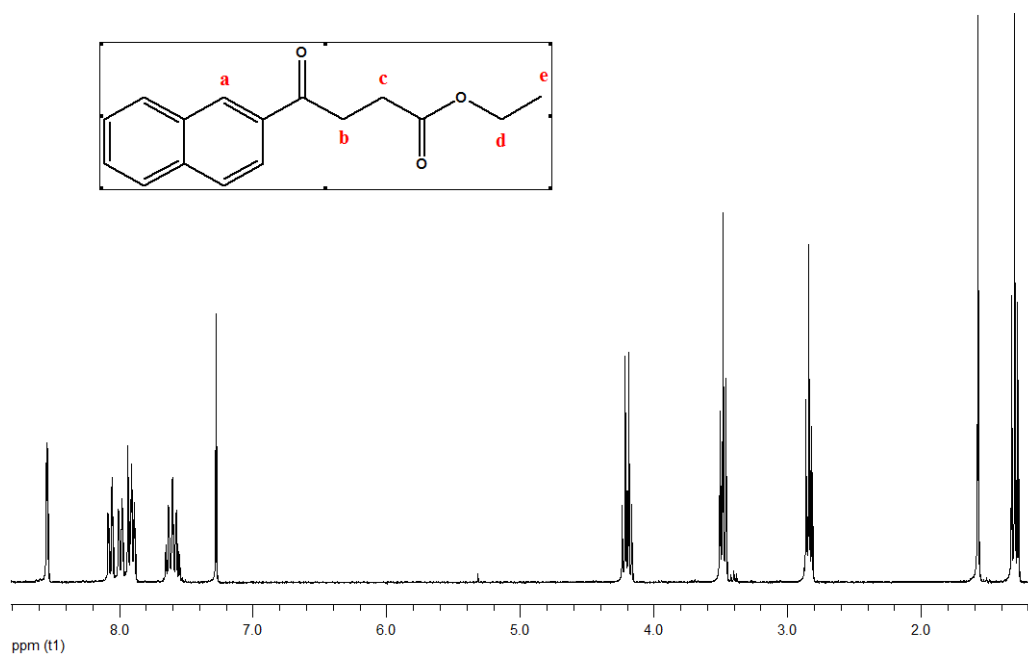


Fig. S8 ¹H NMR of ethyl 4-(2-naphthyl)-4-oxobutanoate in CDCl₃. The structure is reported in the inset.

SAMs characterization

The formation of the film was monitored by cyclic voltammetry using $K_3[Fe(CN)_6]$ as the redox-active probe. When the gold foil is not functionalised, 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 (Fig. S9).

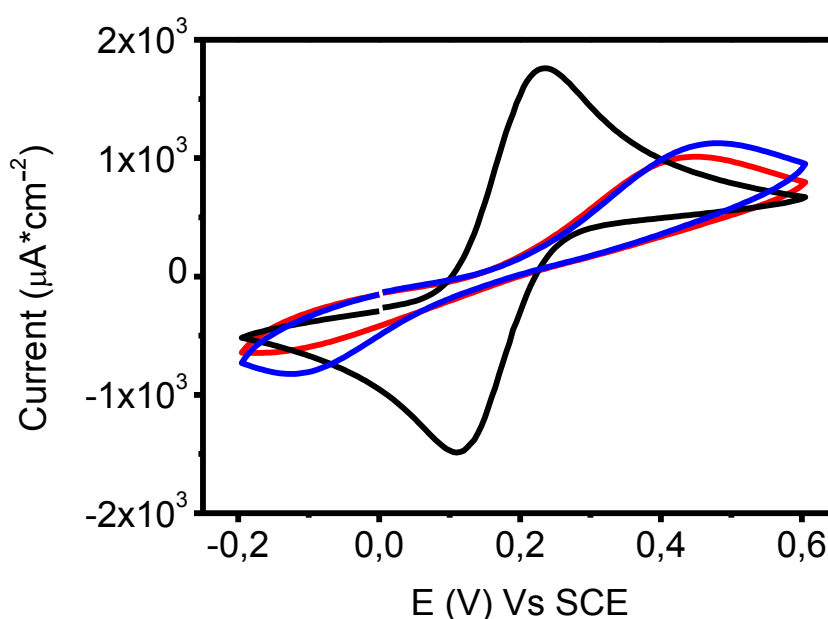


Fig. S9 CV of $K_3[Fe(CN)_6]$ 50 mM in water using as working electrode a clean gold foil (black line) or densely packed SAMs **1** (red line) and **2** (blue line) on gold. Curves are corrected for the immersed area.

Quantitative data on the density of the porphyrin film were obtained by the DPV on the modified electrodes. These experiments were carried out in a 0.1 M solution of Na_2SO_4 in water. The integration of the oxidative peak on the graph afforded 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 tetraferrocenyporphyrins), 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:

$$Q = \frac{\Delta x}{V_s} \sum y_i$$

where y_i are the intensities in Ampere, Δx is the fixed difference in Volts between two experimental points (5 mV) and V_s is the scan rate.

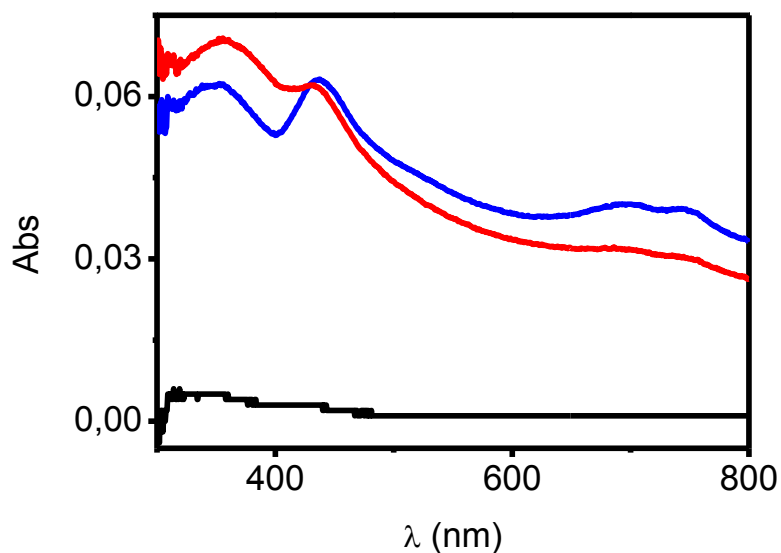


Fig. S10 Comparison between the absorption spectra of **3** (red line) and **4** (blue line) with a bare ITO-supported glass after immersion in a H_2TFcP solution 1mM for 20 hours (black line).

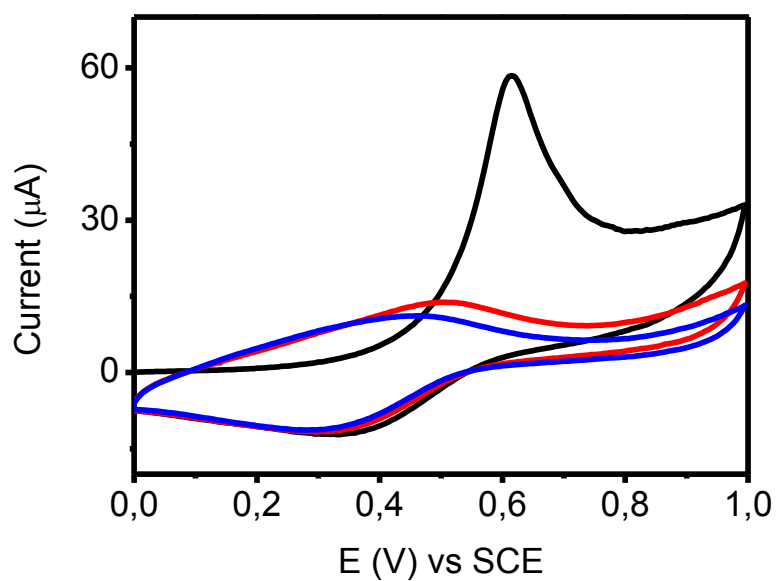


Fig. S11 Subsequent CV scans in $\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$ 0.1 M of SAM **4**. The presence of H_2Tfcp was observed only during the first scan (black line).

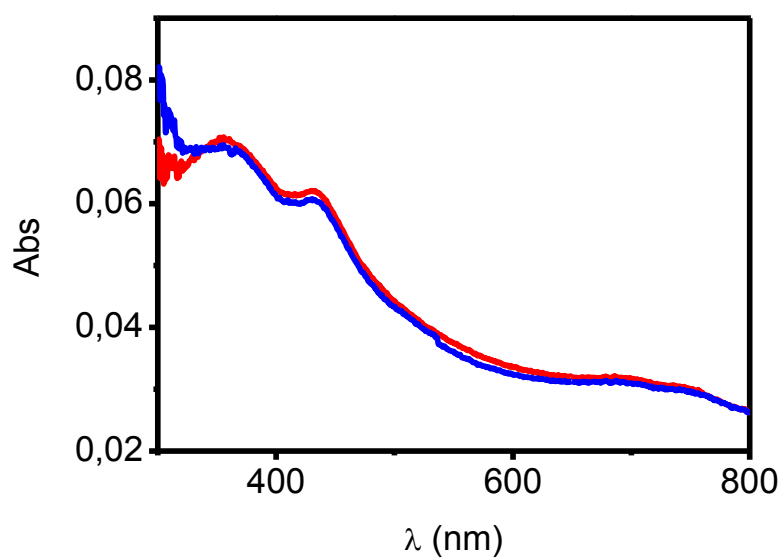


Fig. S12 Comparison between absorption spectra of **3** before (red line) and after (blue line) DPV experiments.

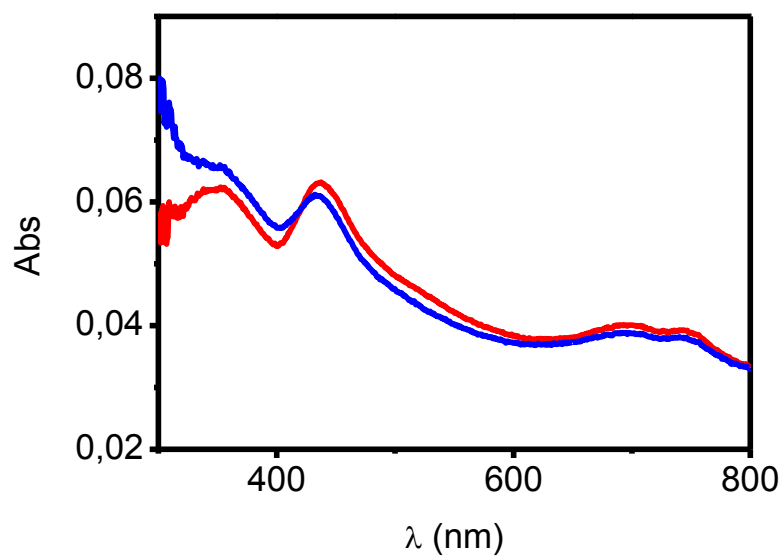


Fig. S13 Comparison between absorption spectra of **4** before (red line) and after (blue line) DPV experiments.

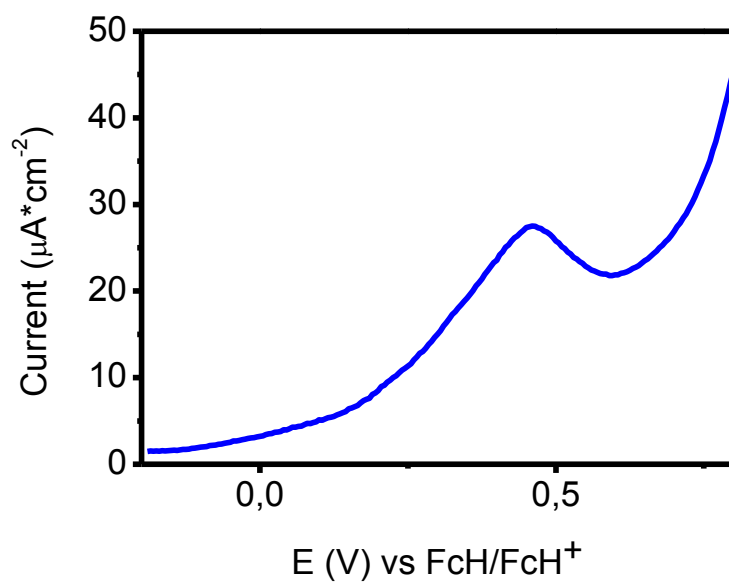


Fig. S14 DPV in $\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$ 0.1 M using a bare gold electrode after immersion in a H_2TFcP solution 1 mM for 20 hours.

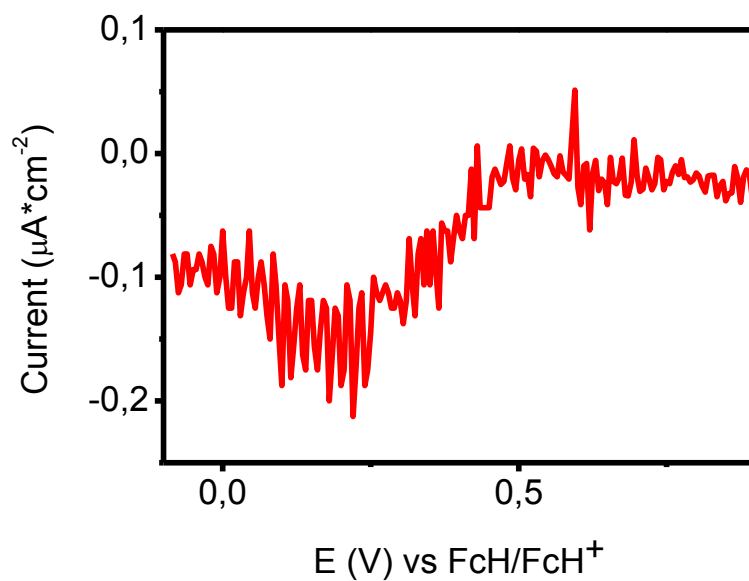


Fig. S15 DPV in $\text{H}_2\text{O}/\text{Na}_2\text{SO}_4$ 0.1 M using a bare ITO electrode after immersion in a H_2TFcP solution 1 mM for 20 hours.

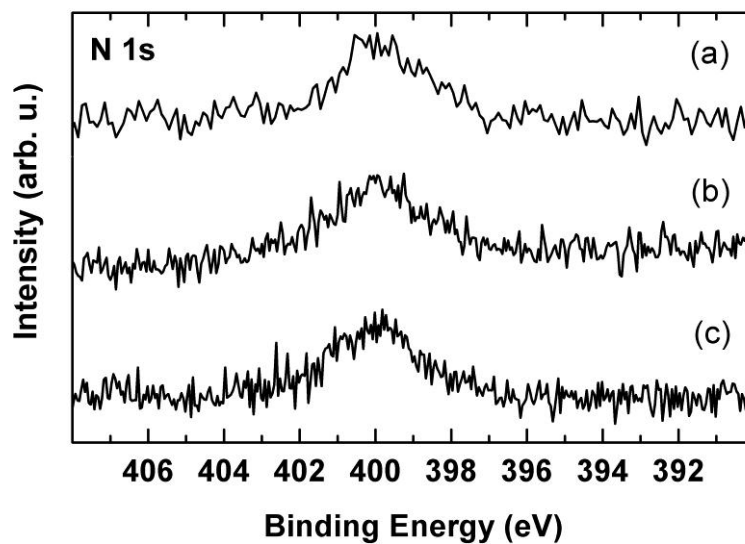


Fig. S16 XPS experimental spectra of N 1s region of SAMs **2** (a), **1** (b) and **4** (c) at $\theta = 71^\circ$.

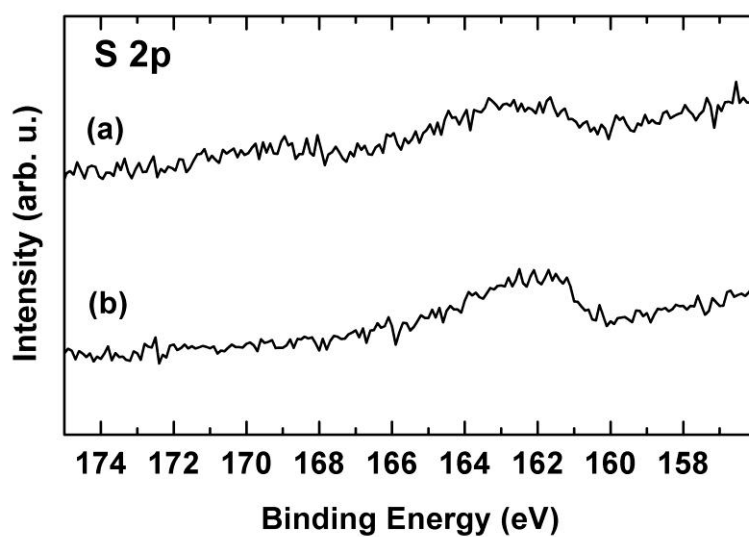


Fig. S17 XP experimental spectra of S 2p region of SAMs **2** (a) and **1** (b) $\theta = 11^\circ$.

Bibliography

- [1] G. Filippini, Y. Israeli, F. Goujon, B. Limoges, C. Bonal and P. Malfreyt, *J. Phys. Chem. B*, 2011, **115**, 11678.