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Synthesis of Thioacetate-Functionalized Cobalt(II) Porphyrins and Their Immobilization on Gold Surface – Characterization by X-ray Photoelectron Spectroscopy

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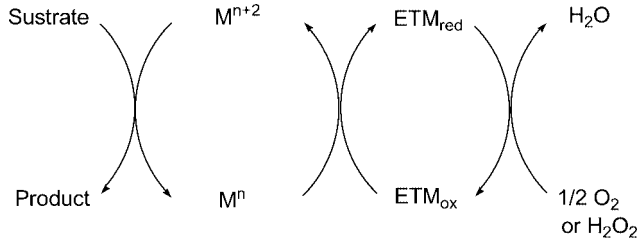
Cobalt tetraarylporphyrins **1-Co** and **2-Co** with thioacetate-functionalized carbon chains on the aryl groups were synthesized. The cobalt porphyrin **2-Co** was immobilized on a gold surface after deprotection of the *S*-acetyl group. The immobilized porphyrin was studied by X-ray Photoelectron Spectroscopy (XPS) and the results suggest that a complete monolayer of porphyrins is formed.

Introduction

Metal-catalyzed oxidation of organic compounds is a continuously growing area of interest in organic chemistry with many applications in industrial processes.[1] However, there is an increased need for cleaner ("greener") technologies, which are based on oxidation by molecular oxygen or aqueous hydrogen peroxide. These oxidants are atom economic and produce only water as the by-product. Direct oxidation of organic substrates with these oxidants is usually inefficient and often proceeds in a non-selective manner. However, in the presence of a suitable substrate-selective redox catalyst, like in nature,[2] combined with one or several relaying redox-couples (*electron-transfer mediators*, ETMs) the oxidation proceeds faster and in a selective manner via the recycling of the components by O_2 or H_2O_2 (Scheme 1).[3]

Macrocyclic metal complexes, in particular metalloporphyrins have attracted attention as biomimetic catalysts in oxidation reactions.[4] Most oxidations with metalloporphyrins have been carried out with oxidants such as iodosobenzene,[4f–4h] periodide,[4e] hypochlorite[5] and molecular oxygen.[4a–d,4i–j,6] Based on the oxygen-activating properties of the metalloporphyrins, mild biomimetic Pd^{II}-catalyzed oxidations have also been developed.[6a] The most remarkable feature of this system is that electrons from Pd^0 are passed through a benzoquinone-hydroquinone redox couple to the oxidized form of the metal porphyrin (or to a related metal macrocycle). The electron transfer between the hydroquinone and the oxidized form of the metal porphyrin is usually slow compared to the other electron transfer steps. A solution to the latter problem was to employ a quinone-functionalized porphyrin.[7] This, indeed, improved the rate of the oxidation reaction, but still did not solve the problem of oxidative dimerization. Moreover, metal porphyrins have several disadvantages in these catalytic systems. They have low solubility in most organic solvents, they can readily dimerize and they degrade in acidic media. In order to overcome the problem of the deactivation, originating from the homogeneous condition, we decided to study the surface-immobilization of the metal porphyrin.



Scheme 1. Biomimetic oxidation involving electron-transfer mediator (ETM).

Porphyrins have been covalently bound to various kinds of surfaces[8] such as silicon,[9] silica,[10] and polymers[11] and gold[12] and they were also encapsulated in zeolites.[13] The most intensively studied and successful existing meth-

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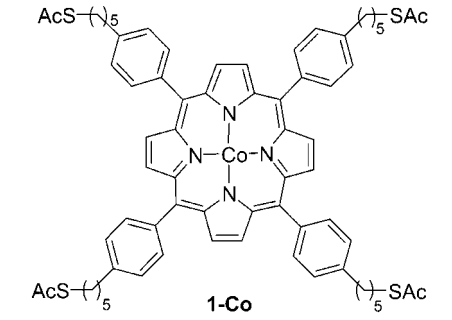
ods are based on the sulfur–gold linkages, and a large number of porphyrin monomers bearing thiols have been prepared.[14] In order to avoid the problems associated with disulfide formation the thiol is best handled in a protected form.[15] It has been reported that *S*-acetyl, *S*-cyano, *S*-(*N*-ethylcarbamoyl) protecting groups undergo cleavage in-situ on gold electrodes.[14k] In the present report we have prepared thiol-functionalized cobalt porphyrins as their *S*-acetyl-protected derivatives and studied their attachment to a gold surface.

The prevalent synthetic routes to porphyrin thioacetates comprise the derivatization of the substituted porphyrins with a suitable reagent to thioacetate unit.[14] Alternatively, there are routes present in the literature where *S*-acetyl-derivatized benzaldehyde-thiols were converted into the corresponding porphyrins,[14] which upon alkaline hydrolysis afforded the free thiols. The *S*-acetyl-protected porphyrin can be metallated by standard procedures.[14k,15,16] In this paper, we present both approaches towards *S*-acetyl functionalized cobalt(II) porphyrins containing four *S*-acetyl-protected linkers (**1-Co** and **2-Co**, Figure 1) and an efficient route to the formation of cobalt(II) porphyrin monolayers on gold surface. These nanostructured functional materials are of growing interest for the rational design and their use in electronic optical and biosensor applications.[17]



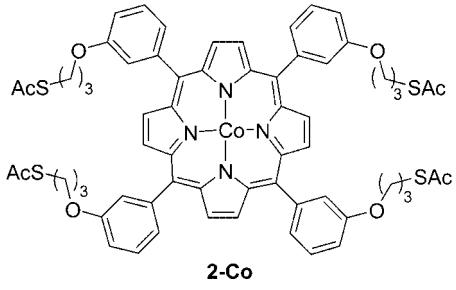


Figure 1. Thioacetate-functionalized cobalt(II) porphyrins for immobilization on gold surface.

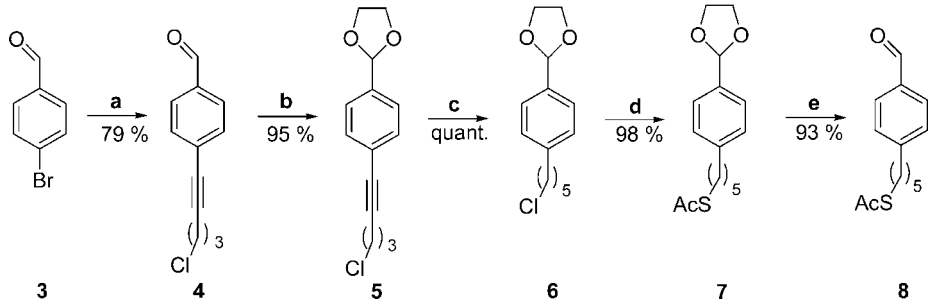
Results and Discussion

Synthesis of Thioacetate-Functionalized Cobalt(II) Porphyrins: The first step towards the synthesis of the porphyrin of **1-Co** was a palladium-catalyzed Sonogoshira coupling between 4-bromobenzaldehyde, (**3**) and 5-chloro-1-pentyne, yielding 4-(5-chloro-1-pentynyl)benzaldehyde (**4**) in 79% yield (Scheme 2). Attempts to use 4-chlorobenzaldehyde were unsuccessful and did not lead to the desired product. The aldehyde **4** was protected as the acetal to prevent side reactions in the subsequent steps. The alkyne functionality was reduced via a $RhCl(PPh_3)_3$-catalyzed hydrogenation to give a quantitative yield of **6**. The thioacetate was subsequently introduced via a nucleophilic displacement of the chloride by KSAc to furnish **7** in 98% yield. Deprotection of the acetal afforded the desired aldehyde **8** in 93% yield.

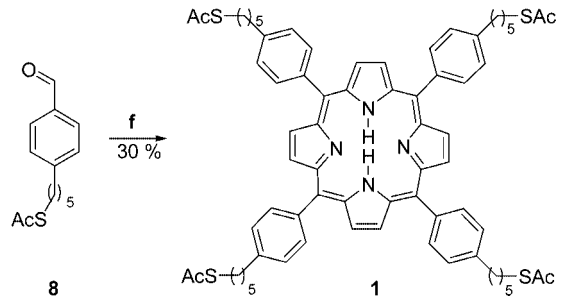
The synthesis of the *S*-acetyl protected porphyrin **1** was carried out according to the method developed by Lindsey[14k] (Scheme 3), in which trifluoro acetic acid was used to catalyze the condensation of the freshly distilled pyrrole with **8**.

Two routes were examined for the synthesis of **2**, as is shown in Scheme 4. The first route involved the synthesis thiol-aldehyde **11** followed by the acid-catalyzed condensation of **11** with pyrrole. The latter condensation resulted in 34% yield of *S*-acetyl-protected thiol-porphyrin **2**.[14k] The synthesis of **11** involved the reaction of 1,3-dibromopropane with 3-hydroxybenzaldehyde (**9**) to give bromide **10**, followed by quantitative substitution of the bromide in **10** with potassium thioacetate, to produce **11** (Scheme 4).

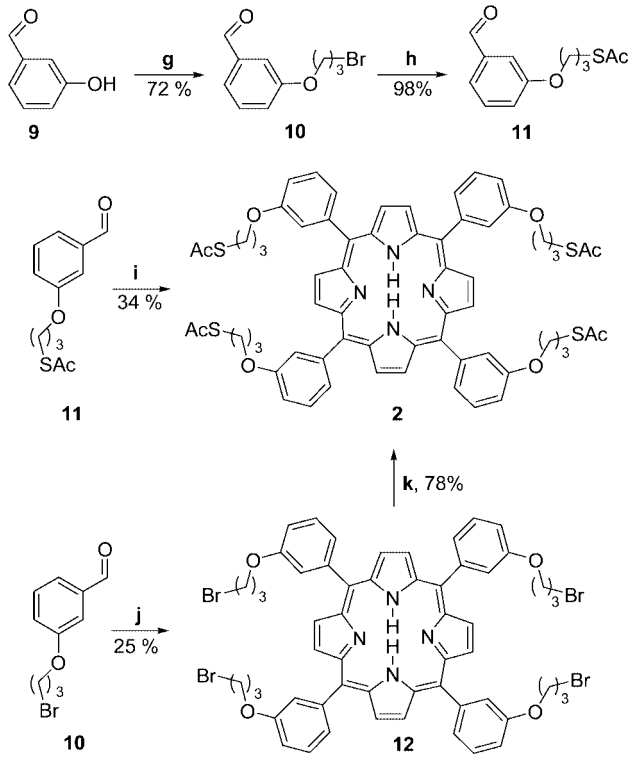
Alternatively, porphyrin **2** was synthesized via porphyrin **12**, which was obtained from aldehyde **10** and pyrrole in a 25% yield. Subsequent substitution of all four bromides in **12** with potassium thioacetate afforded **2** in 78% yield.



Scheme 2. Reagents and conditions: **a**. 5-chloro-1-pentyne, $Pd(OAc)_2$, PPh_3, NEt_3, CuI, THF, room temp. overnight; **b**. ethylene glycol, TsOH, benzene, reflux, 12 h; **c**. $RhCl(PPh_3)_3$, H_2, benzene, room temp. 14 h; **d**. KSAc, reflux, 13 h, 56 °C; **e**. TsOH, acetone, H_2O, reflux, 14 h.



Scheme 3. Reagents and conditions: **l**. 1: pyrrole, TFA, DCM, room temp., 1.5 h, 2: *p*-chloranil, reflux, 1 h.



Scheme 4. Reagents and conditions: **g**. 1,3-diromopropane, NaOH, H_2O, room temp., 24 h; **h**. KSAc, THF, reflux, 16 h. **i**. 1: pyrrole, TFA, DCM, room temp., 1.5 h, 2: *p*-chloranil, reflux 1 h; **j**. 1: pyrrole, TFA, DCM, room temp., 1.5 h, 2: *p*-chloranil, reflux 1 h; **k**. KSAc, THF, reflux 40 h.

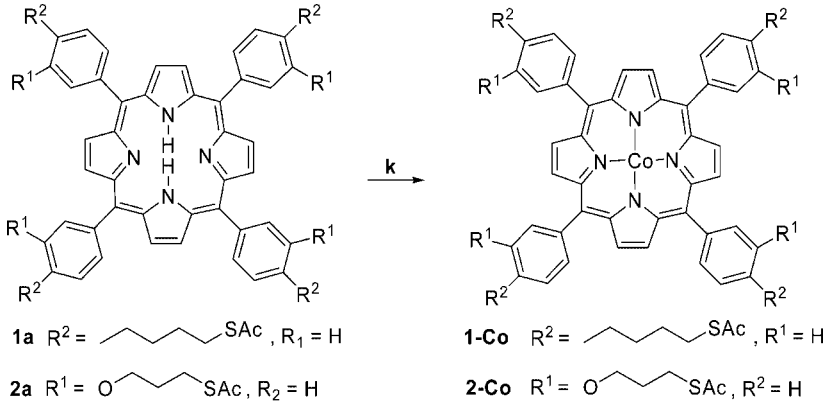
Preparations of **1-Co** and **2-Co** were conducted quantitatively by direct metallation of **1** and **2** with $Co(OAc)_2{\cdot}4H_2O$ by standard literature procedure (Scheme 5).[14k]

X-ray Photoelectron Spectroscopy Study of the Immobilized Co^{II} Porphyrin Layers: Immobilized Co-porphyrin layers were prepared by acidic deprotection of **2-Co** to give **13-Co** followed by the immobilization on a gold surface (Scheme 6). The resulting porphyrin layers were studied by means of X-ray Photoelectron Spectroscopy (XPS).

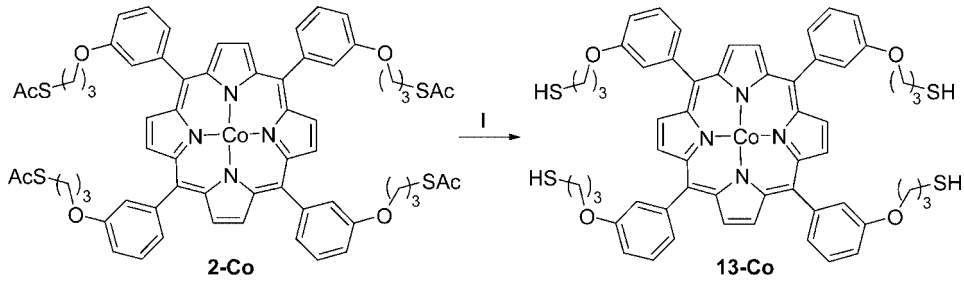
In Figure 2 (a) a survey photoelectron spectrum of the bare Au surface obtained at a take off angle (TOA) of 10° of the emitted photoelectrons is presented. No additional contaminants besides residual carbon and oxygen could be detected.

Figure 2 (b) shows a survey spectrum at a TOA of 10° for the deprotected **2-Co** porphyrins **13-Co** deposited on the Au surface. The spectrum of the sample after molecular deposition looks different, and shows additional features compared to the spectrum of the bare Au surface. The new peaks appearing in the spectrum can be related to the different atomic constituents of the molecule. The intensity ratio in the spectrum for N, S and Co agrees, within the statistical error with the molecular stoichiometry. Higher intensity than expected is detected for carbon and oxygen.[18] The slightly too high intensity of carbon can be explained by the contamination of the bare Au surface and additional air contamination of the molecular layer during mounting the sample and introducing it into the load-lock chamber of the XPS instrument. The same considerations can be applied to explain the too high intensity detected for oxygen, i.e. it is very likely that oxygen adsorbs to the cobalt-center of the **13-Co** molecule. The high oxygen signal can also be related to a not-completed deprotection of the **2-Co** molecules. However, the oxygen contamination makes it difficult to give a quantitative estimation of the yield for the deprotection Scheme used.

The data shown in Figure 2 (b) corresponds to a deposition time in the order of 20 hours. For longer deposition times the same results with non-increasing spectral intensity were obtained. Consequently, saturation of the molecular layer on the Au surface is reached, i.e. the growth stops after an initial layer. The molecular coverage has been cal-



Scheme 5. Reagents and conditions: **k**. $Co(OAc)_2{\cdot}4H_2O$, DCM/MeOH, 4:1, reflux, 2 h.



Scheme 6. Reagents and conditions: **I**. $HCl_{(aq.)}$, DMF, room temp.

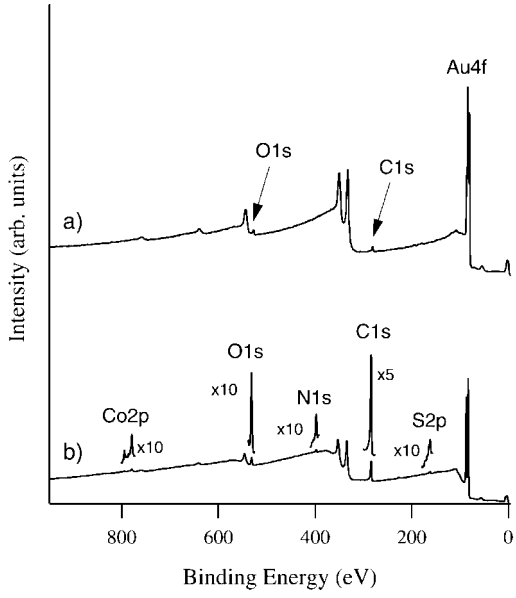


Figure 2. a) Photoelectron spectrum obtained at a take off angle (TOA) of 10° of the bare Au surface prior to molecular deposition. The peaks corresponding to carbon and oxygen contamination are marked. All other features in the spectrum are related to the Au substrate. The most intensive photoemission line for Au is also marked (Au4f). b) Photoelectron spectrum at a TOA of 10° of **13-Co** (deprotected **2-Co**) on the Au surface. The different atomic constituents of the molecule are present and marked in the spectrum.

culated using the XPS data. The result corresponds to the formation of a complete monolayer. These findings suggest that a complete monolayer of porphyrins is formed in analogy to the results obtained for self-assembled monolayers (SAM) on Au surfaces.[12a]

Figure 3 illustrate the immobilization of the cobalt porphyrin **13-Co** (deprotected **Co-2**) to the gold surface.

Conclusions

We have successfully prepared **1-Co** and **2-Co** in relatively good overall yields, by acid-catalyzed condensation of the corresponding *S*-acetyl-functionalized benzaldehydes and pyrrole followed by direct metallation of the porphyrins. Moreover, an alternative route is presented for **2-Co** via the derivatization of the corresponding bromo-functionalized porphyrin **12**. After deprotection of the cobalt(II) porphyrin **2-Co** a complete porphyrin monolayer on Au surface was formed, as indicated by the XPS results.

Experimental Section

General Procedures: ^1H NMR and ^{13}C NMR spectra were measured on a Varian Mercury (300 MHz or 400 MHz and at 75 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent, if not otherwise specified. Chemical shifts (δ values) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δ_H = 7.26 and δ_C 77.0) as internal standards, coupling constants (*J*) are given in Hz and without signs. Flash column chromatography was performed by use of 60 Å (35–70 μm) silica gel. MALDI mass spectra were obtained on a Finnegan-MAT GCQ four sector mass spectrometer using 3-nitrobenzyl alcohol as matrix. UV/Vis spectra were recorded on a Varian Cary 50 spectrophotometer. XPS measurements have been performed in a Scienta ESCA 300 spectrometer using monochromized Al-K_α X-rays with a photon energy of 1487 eV.

Materials: All reagents were purchased from commercial suppliers and used without further purification. CH_2Cl_2, diisopropylethylamine and triethylamine were distilled from CaH_2. Pyrrole was dis-

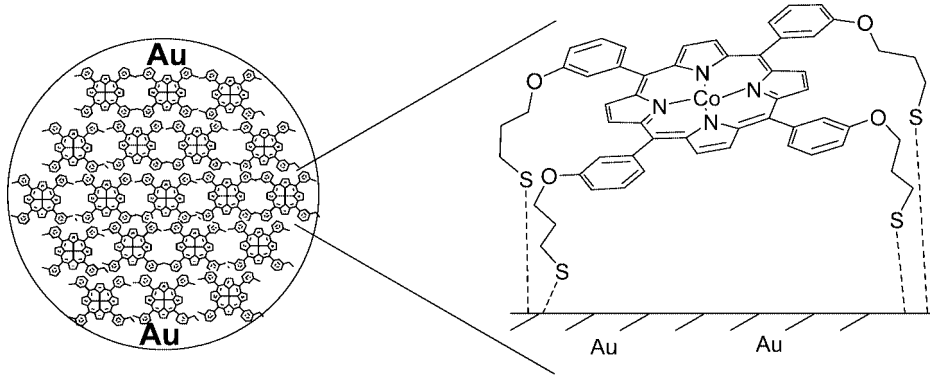


Figure 3. Immobilization of cobalt porphyrin on a gold surface via sulfur tails.

tilled prior to use. DMF was dried on CaH_2 overnight then distilled under vacuum prior to use.

Polycrystalline gold films on Si(100) wafers were prepared by thermal evaporation of a Cr adhesion layer (about 10 nm) followed by thermal evaporation of about 150 nm of gold. These substrates were cleaned in piranha solution [H_2SO_4:H_2O_2 30% (v/v), 2:1] and rinsed with ultra pure water. Finally, the substrates were blow dried with Ar. No additional contaminants could be detected in the XPS besides a low amount of residual carbon and oxygen.

The smoothness of the clean surfaces was checked by atomic force microscopy (AFM). Images with a scan range of 1 μm × 1 μm were taken at different spots on the surface in order to determine the surface roughness. The resulting root mean square (RMS) is about 2.9 nm.

4-(5-Chloro-1-pentynyl)benzaldehyde (4): Triphenylphosphane (280 mg, 1.06 mmol), $Pd(OAc)_2$ (108 mg, 0.48 mmol), triethylamine (4.4 mL, 31.3 mmol) and CuI (122 mg, 0.64 mmol) were dissolved in 50 mL of THF under argon atmosphere. 4-Bromobenzaldehyde (1.85 g, 10.0 mmol) was added via a syringe, followed by dropwise addition of 5-chloro-1-pentyne (1.052 mL, 10.0 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (pentane/ethyl acetate, 85:15) to give 1.64 g (79%) of **4**. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 2.07 (t, J = 7 Hz, 2 H), 2.64 (t, J = 7 Hz, 2 H), 3.70 (t, J = 6 Hz, 2 H), 7.51 (d, J = 8 Hz, 2 H), 7.80 (d, J = 9 Hz, 2 H), 9.97 (s, 1 H). ^{13}C NMR ($CDCl_3$, 20 °C): δ = 17.21, 31.42, 43.82, 81.18, 92.98, 129.73, 130.20, 132.36, 135.40, 191.65. Compound **4** was characterized by comparison with spectroscopic data reported in ref.[19] (ref.[19] reports ^{1}H and ^{13}C NMR in CD_2Cl_2, which are almost identical to those reported here).

2-[4-(5-Chloro-1-pentynyl)phenyl]-1,3-dioxolane (5): *p*-Toluenesulfonic acid monohydrate (151 mg, 0.80 mmol) was dissolved in 12 mL of benzene. Aldehyde **4** (1.64 g, 7.9 mmol) and ethylene glycol (2.2 mL, 39.4 mmol) were added via syringe. The resulting mixture was refluxed under Dean–Stark condition for 12 h. The reaction mixture was washed three times with 15 mL of saturated $NaHCO_3$ solution. The organic phase was dried with K_2CO_3, and the solvent was removed under reduced pressure to give 1.80 g (95%) of **5**. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 2.06 (p, J = 7 Hz, 2 H), 2.61 (t, J = 7 Hz, 2 H), 3.71 (t, J = 6 Hz, 2 H), 4.00–4.14 (m, 4 H), 5.79 (s, 1 H), 7.4 (s, 4 H). ^{13}C NMR ($CDCl_3$, 20 °C): δ = 17.11, 31.65, 43.95, 65.53, 81.49, 88.90, 103.57, 124.67, 126.59, 131.81, 137.65.

2-[4-(5-Thioacetoxypentyl)phenyl]-1,3-dioxolane (7): Compound **5** (947 mg 3.78 mmol) and $RhCl(PPh_3)_3$ (70 mg, 0.075 mmol) were dissolved under hydrogen atmosphere in 20 mL benzene. After 14 h of stirring at room temperature the reaction was complete according to ^{1}H NMR spectra and the benzene was evaporated to give **6** as a solid, which was used in the subsequent step without further characterization. The remaining solid **6** was dissolved in 70 mL of acetone and potassium thioacetate (0.843 g, 7.4 mmol) was added at once. The resulting mixture was refluxed for 13 h. The solid residue was filtered off, followed by the evaporation of the acetone. The remaining solid was dissolved in 400 mL diethyl ether and extracted with water (3 × 400 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed under vacuum to yield 1.084 g (98%) of **7**. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 1.40 (m, 2 H), 1.62 (m, 4 H), 2.31 (s, 3 H), 2.68 (t, J = 7 Hz, 2 H), 2.85 (t, J = 7 Hz, 2 H), 7.32 (d, J = 8 Hz, 2 H), 7.79 (d, J = 8 Hz, 2 H), 9.97 (s, 1 H). ^{13}C NMR ($CDCl_3$, 20 °C): δ = 28.53, 29.13, 29.56, 30.70, 30.86, 36.18, 129.29, 130.15, 134.72, 150.15, 192.20, 196.23.

3-(3-Formylphenoxy)propyl Bromide (10):[20] 3-Hydroxybenzaldehyde (**9**) (18.3 g, 150 mmol) was dissolved in a 75 mL aqueous solution of sodium hydroxide (150 mmol). After flushing with argon, 36.3 g (180 mmol) 1,3-dibromopropane was added and the reaction mixture was stirred vigorously, over a 24-hour period under reflux. The mixture was cooled, the layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 40 mL). The non-aqueous layers were combined, washed with four 50 mL portions of 2.0 M aqueous sodium hydroxide, once with 50 mL 2.0 M HCl, and with two 50 mL portions of water. The organic layer was dried ($MgSO_4$) and concentrated. The product was purified by distillation to give an analytically pure sample of **10** in a yield of 72%. ^{1}H NMR (300 MHz): δ = 9.97 (s, 1 H), 7.45–7.38 (m, 3 H), 7.17 (m, 1 H), 4.16 (t, 2 H, J = 6.0 Hz), 3.60 (t, 2 H, J = 6.3 Hz), 2.34 (m, 2 H). ^{13}C NMR (75.4 MHz): δ = 192.3, 159.5, 138.1, 130.3, 123.9, 122.1, 113.1, 65.8, 32.4, 30.0; m/z for $C_{10}H_{11}BrO_2$ ([M]): 241.99 (calcd. 241.9942).

Thioacetate 11: Bromide **10** (12.4 g, 51.2 mmol) and potassium thioacetate (11.7 g 102.3 mmol) were dissolved in 100 mL of dry THF and the mixture was refluxed for 16 hours. After cooling to ambient temperature, the reaction mixture was filtered to remove precipitates and the solvent of the filtrate was evaporated in vacuo. The dark brown oil was dissolved in 75 mL diethyl ether and washed twice with 75 mL of brine. The organic layer was dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The product was purified by flash chromatography (silica, pentane/diethyl ether, 4:1) to yield 12.0 g (98%) of thioacetate **11**. ^{1}H NMR (300 MHz): δ = 9.96 (s, 1 H), 7.45–7.42 (m, 2 H), 7.37 (m, 1 H), 7.16 (m, 1 H), 4.06 (t, 2 H, J = 6.0 Hz), 3.06 (t, 2 H, J = 6.9 Hz), 2.33 (s, 3 H), 2.09 (m, 2 H). ^{13}C NMR (75.4 MHz): δ = 195.8, 192.3, 159.6, 138.0, 130.3, 123.8, 122.1, 113.0, 66.7, 30.9, 29.4, 26.0; m/z for $C_{12}H_{14}O_3S$ ([M]): 238.0669. (calcd. 238.0664).

5,10,15,20-Tetrakis[4-(5-thioacetoxypentyl)phenyl]porphyrin (1). General Porphyrin Synthesis: Compound **7** (1074 mg, 3.65 mmol) and *p*-toluenesulfonic acid monohydrate (138 mg, 0.73 mmol) were dissolved in a mixture of 15 mL of acetone and 2.3 mL of H_2O and refluxed for 14 h. The solvent mixture was evaporated under reduced pressure and the solid residue was separated with column chromatography with (pentane/ethyl acetate, 95:5), yielding 0.981 g (93%) of 4-(5-thioacetoxypentyl)benzaldehyde (**8**). Aldehyde **8** was used directly for the next step. Pyrrole (1.50 mL, 21.6 mmol) and aldehyde **8** (5.4 mL, 21.6 mmol) were dissolved in 500 mL dichloromethane. Under argon atmosphere a solution of trifluoroacetic acid (1.65 mL, 21.6 mmol) in 10 mL dichloromethane was slowly added. The reaction mixture was stirred for 1.5 hours in the dark under argon, during which time it turned dark purple. *p*-Chloranil (3.98 g, 16.2 mmol) was added and the mixture was refluxed for 1 hour. After the mixture was cooled to ambient temperature, triethylamine (3.0 mL, 21.6 mmol) was added in order to neutralize the solution. The reaction mixture was filtered and the volume reduced to approximately 50 mL. The product was purified using column chromatography (silica, CH_2Cl_2) to yield the porphyrin derivative **1** (1.92 g, 1.62 mmol, 30%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = –2.73 (br. s, 2 H), 1.64 (m, 8 H), 1.77 (m, 8 H), 1.93 (m, 8 H), 2.38 (s, 12 H), 2.96 (t, J = 7 Hz, 8 H), 3.00 (t, J = 7 Hz, 8 H), 7.54 (d, J = 7 Hz, 8 H), 8.13 (d, J = 7 Hz, 8 H), 8.87 (s, 8 H). m/z for $C_{72}H_{77}N_4O_4S_4$ ([M]): 1191.27. UV (CH_2Cl_2): λ_{abs} = 420, 516, 553, 599, 649 nm.

5,10,15,20-Tetrakis[3-(3-thioacetoxypropoxy)phenyl]porphyrin (2): Prepared according to the general method from **11** (5.15 g, 21.6 mmol) and pyrrole (1.50 mL, 21.6 mmol) which afforded the porphyrin derivative **2** (2.3 g, 2.0 mmol, 34%). Alternatively, por-

phyrin **12** (1.14 g, 0.981 mmol) and potassium thioacetate (671 mg, 5.88 mmol) were dissolved in 50 mL dry THF and the mixture was refluxed for 40 hours. After cooling to ambient temperature, the reaction mixture was filtered and the solvent was evaporated in vacuo. The porphyrin was dissolved in 50 mL dichloromethane and washed two times with 75 mL water. The organic layer was dried with sodium sulfate, filtered and the evaporated to dryness. The product was purified using column chromatography (silica, dichloromethane) to yield porphyrin **2** (0.76 mmol, 0.87 g, 78%). ^{1}H NMR (300 MHz): δ = 8.92 (s, 8 H), 7.84 (d, 4 H, J = 7.8 Hz), 7.79 (s, 4 H), 7.65 (t, 4 H, J = 7.8 Hz), 7.33 (d, 4 H, J = 8.1 Hz), 4.22 (t, 8 H, J = 6.0 Hz), 3.14 (t, 8 H, J = 7.2 Hz), 2.32 (s, 12 H), 2.17 (m, 8 H), –2.78 (s, 2 H). ^{13}C NMR (75.4 MHz): δ = 195.9, 157.4, 143.7, 132.2–130.7, 128.1, 127.8, 121.4, 120.1, 114.4, 66.7, 30.9, 29.7, 26.2. UV (CH_2Cl_2): λ_{abs} = 418, 514, 549, 589, 646 nm.

5,10,15,20-Tetrakis[3-(3-bromopropoxy)phenyl]porphyrin (12): Prepared according to the general porphyrin synthesis from pyrrole (1,50 mL, 21.6 mmol) and **10** (5,25 g, 21.6 mmol) to give **12** (1.55 g, 1.33 mmol, 25%). ^{1}H NMR (300 MHz): δ = 8.90 (s, 8 H), 7.84 (d, 4 H, J = 7.8 Hz), 7.79 (s, 4 H), 7.65 (t, 4 H, J = 7.8 Hz), 7.34 (d, 4 H, J = 8.1 Hz), 4.30 (t, 8 H, J = 6.3 Hz), 3.68 (t, 8 H, J = 6.3 Hz), 2.41 (m, 8 H), –2.80 (s, 2 H). ^{13}C NMR (75.4 MHz): δ = 157.3, 143.7, 131.8–130.5, 128.1, 127.8, 121.4, 120.0, 114.3, 65.8, 32.8, 30.2. UV (CH_2Cl_2): λ_{abs} = 419, 514, 551, 591, 646 nm.

5,10,15,20-Tetrakis[4-(5-thioacetoxypentyl)phenyl]porphyrincobalt-(II) (1-Co). General Procedure: Porphyrin **1** (119 mg, 0.1 mmol) was dissolved in 20 mL of a 4:1 mixture of CH_2Cl_2 and MeOH under argon atmosphere. $Co(OAc)_2{\cdot}4H_2O$ (30.6 mg, 0.12 mmol) was added and the resulting reaction mixture was refluxed for 2 h. The formation of **1-Co** was confirmed by UV spectroscopy. Yield: 112 mg, 98%. UV (CH_2Cl_2): λ_{abs} = 412, 530 nm.

5,10,15,20-Tetrakis[3-(3-thioacetoxypropoxy)phenyl]porphyrincobalt(II) (2-Co): Prepared according to the general procedure from 114 mg (0.1 mmol) of porphyrin **2** and 30.6 mg (0.12 mmol) of $Co(OAc)_2{\cdot}4H_2O$ in 20 mL of 4:1 mixture of CH_2Cl_2 and MeOH to give 117 mg (98%) of **2-Co**. UV (CH_2Cl_2): λ_{abs} = 410, 529 nm.

Immobilization of 2-Co on a Gold Surface: The evaporated gold substrates on Si wafers were cleaned in Piranha solution [H_2SO_4:H_2O_2 (30% aq.), 2:1] and rinsed with ultra pure water prior to molecular deposition. The Au surface was checked for remaining contaminants by means of XPS. A solution of 0.5 mM **2-Co** in *N*,*N*-dimethylformamide (DMF) was prepared. Deprotection of the *S*-acetyl groups was performed by adding 40 molar excess of HCl. After an initial reaction time in the order of 2 hours for the deprotection to take place, the Au surface was immersed in the molecular solution for typically 20 hours. Then the sample was rinsed with DMF, soaked for 10–20 minutes in DMF, rinsed again with DMF and afterwards with ultra-pure water and finally blow dried in argon. The immobilization was confirmed by XPS.

Surface Coverage Estimation by XPS: The coverage has been calculated by comparing the intensity of the N1s signal to the intensity of the Au4f signal according to ref.[21] Standard cross sections have been used for the calculation. The calculated coverage is 0.67 molcules/nm^2. This corresponds to an area of 150 Å^2 per molecule. This result fits very well to the size of a single porphyrin and corresponds therefore to a full monolayer.

Supplementary Information (see footnote on the first page of this article): General procedures. Copies of ^{1}H and ^{13}C NMR spectra of compounds **1**, **2**, **5**, **7**, **10**, **11**, and **12**. This material is available free of charge via the Internet (http://www.eurjoc.org) or from the author.

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