Inorganica Chimica Acta 361 (2008) 3877–3881

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

NO_2 sensing ability of a monolayer of cobalt(II) porphyrin molecules covalently assembled on a engineered silica substrate

Antonino Gulino *, Placido Mineo, Ignazio Fragalà

Dipartimento di Scienze Chimiche, Università di Catania and I.N.S.T.M. UdR di Catania, Viale Andrea Doria 6, 95125 Catania, Italy

ARTICLE INFO

Article history:
Received 10 January 2008
Accepted 26 February 2008
Available online 5 March 2008

Dedicated to Professor Dante Gatteschi.

Keywords:
Porphyrin
Cobalt
Assembly
UV–Vis
XPS
NO_2

ABSTRACT

The 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl)- and 5,10,15,20-tetrakis-(*p*-dodecanoxyphenyl)-cobalt porphyrin complexes were synthesized, purified and characterized. Silica substrates were functionalized with a covalent 4-$ClCH_2C_6H_4SiCl_3$ monolayer. Additional covalent bonding of the 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl)-cobalt porphyrin to the silylated substrates was further achieved. The monolayer surface chemical characterization was carried out by X-ray photoelectron measurements. Both the Co 2p and N 1s spectra are evident. The NO_2 sensing capability of the present cobalt porphyrin systems, at ppm levels, has been demonstrated.

1. Introduction

There is an increasing technological interest in the synthesis of hybrid inorganic/organic nanomaterials. Syntheses based on covalent assembly of appropriate molecules on suitable inorganic substrates represent one of the most powerful approaches in the perspective of fabrication of devices showing specific single molecule properties and to study functional molecular architectures [1–12].

Many different interesting molecular properties can be investigated by optical measurements, e.g. molecular switching, luminescence quenching, variation in optical absorbance, non-linear optical properties, and molecular recognition properties. In these cases, transparent silica (quartz) substrates are very useful for covalently assembling of functional molecules. The typical synthesis procedure requires first covalent substrate grafting with a given bi-functional appropriate coupling layer (CL) that can bond both to the substrate and to the following functional molecules [11].

Cobalt nanomaterials play a dominant role in numerous bio- and physico-chemical processes [12]. Cobalt porphyrins exhibit many interesting properties due to their involvement in electron transfer reactions [13], catalysis [14], sensing [15], optical behavior [16], etc. Despite these numerous applications, the knowledge of their molecular properties at the solid state is crucial and remains a challenge for both scientific and technologic reasons [17–20]. In this perspective, the covalent immobilization of a mono- or sub-layer of these molecules on a transparent solid substrate probably represents the most suited prerequisite to accomplish this task. To this purpose, well-tailored cobalt porphyrin molecules, having peripheral substituents that increase the steric hindrance, should avoid aggregation phenomena [1] [21] so that the molecular, instead of bulk, properties should be emphasized. This final goal can be pursued by appropriate chemical synthetic strategies, adopted to obtain the molecular building block, combined with suitable characterization techniques to investigate the engineered substrate.

In this research field, as a part of an on-going study regarding the engineering of silica substrates by covalent bonding of sensing molecules [22–29] the surface evolution of transparent SiO_2 substrates along the step by step grafting of appropriate coupling layer groups suited for successive anchoring of functional molecules [24,30,31] has recently been described. Moreover, we also described the fabrication of highly sensitive and selective optical sensors using different porphyrin monolayers [22–25,27–29].

Therefore, there was enough motivation for us to embark on the synthesis and characterization of a new monolayer of cobalt

---

* Corresponding author. Tel.: +39 095 7385067; fax +39 095 580138.
E-mail address: agulino@dipchi.unict.it (A. Gulino).

[1] The presence of only one hydroxyl group in the peripheral position of the cobalt porphyrin allows a univocal covalent linkage to the substrate. Moreover, the steric hindrance due to the three long aliphatic groups, covalently bounded to the remaining peripheral positions of the porphyrin, should prevent aggregation phenomena.

0020-1693/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2008.02.055

porphyrin molecules covalently assembled on a functionalized silica surface.

2. Experimental details

2.1. Synthesis and characterization of porphyrin cobalt complexes

Aldrich grade reagents and solvents, some of them packed under nitrogen, were used throughout all the present syntheses. The dodecanoxyphenyl porphyrin derivatives namely 5,10,15-tri-(*p*-dodecanoxyphenyl)-20-(*p*-hydroxyphenyl) porphyrin (R_3PH_2) and 5,10,15,20-tetrakis-(*p*-dodecanoxyphenyl) porphyrin (R_4PH_2) were synthesized, purified and characterized as already reported [32]. Cobalt complexes of R_3PH_2 and R_4PH_2 (hereafter R_3PCo and R_4PCo, respectively) were obtained by reacting appropriate porphyrin derivatives for 4 hours with an excess (1:30 mol/mol) of cobalt(II) acetate tetrahydrate, in pyridine at 100°C, in nitrogen atmosphere. After evaporation of the solvent, the pure product was isolated by column chromatography separation, using silica gel as a stationary phase and a mixture of $CHCl_3/C_2H_5OH/N(C_2H_5)_3$ (97.5/2.0/0.5) as eluant.

The chemical characterization of R_3PCo and R_4PCo was performed by MALDI-TOF mass spectrometry. To this purpose, samples were dissolved in THF, mixed with a 0.4 M THF solution of *trans*-3-indoleacrylic acid (used as a matrix), and loaded on the sample plate. Mass spectra were acquired by a Voyager DE instrument (PerSeptive Biosystem) using a delay extraction procedure (25 kV applied after 2600 ns with a potential gradient of 454.54 V/mm and a wire voltage of 25 V) and a detection in linear mode. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns, 50 Hz) and a flash AD converter (time base 2 ns).

2.2. Synthesis and characterization of the covalently assembled monolayer

Fused silica (quartz) substrates were cleaned by immersion in “piranha” solution (concd. H_2SO_4:30% H_2O_2 70:30 v/v) at 80 °C for 1 h and then left to cool to room temperature. Subsequently, substrates were repeatedly rinsed with double distilled water and immersed in a H_2O:30% H_2O_2:NH_3 5:1:1 v/v/v mixture at room temperature for 40 min [24,28]. Then, these were washed with double distilled water and dried under vacuum immediately before coupling agent deposition. All the successive sample manipulations were performed in a glove box under N_2 atmosphere. In particular, freshly cleaned substrates were immersed, at room temperature for 30 min, in a 1:100 (v/v) *n*-heptane solution of the chemisorptive siloxane, trichloro[4-(chloromethyl)phenyl]-silane ($4\text{-}ClCH_2C_6H_4SiCl_3$) to afford a monolayer of the coupling agent (CA) [24,28]. Then, these were washed with copious amounts of pentane, sonicated 2 min in acetone to remove any physisorbed CA, immersed in a toluene 1.0×10^{-4} M solution of the R_3PCo and heated up to 80 °C under stirring for 48 h. The substrates bearing the covalently self-assembled cobalt porphyrin monolayer (R_3PCo-SAM) were cooled to room temperature and repeatedly washed and sonicated with toluene, THF and CH_2Cl_2 to remove any residual unreacted porphyrin.

X-ray photoelectron spectra (XPS) were measured at 45°, relative to the surface plane with a PHI 5600 Multi Technique System which offers a good control of the electron take-off angle (base pressure of the main chamber 2×10^{-10} Torr) [33,34]. The acceptance angle of the analyzer and the precision of the sample holder concerning the take-off angle are ±3° and ±1°, respectively. The spectrometer is equipped with a dual anode X-ray source; a spherical capacitor analyzer (SCA) with a mean diameter of 279.4 mm; an electrostatic lens system Omni Focus III. Samples were mounted on Mo stubs. Spectra were excited with Al Kα radiation. The structure due to the $K\alpha_2$ satellite radiation has been subtracted from the spectra before the data processing. The XPS peak intensities were obtained after Shirley background removal [35]. Procedures to account for steady state charging effect have been described elsewhere [33,34]. Experimental uncertainties in binding energies lie within ±0.45 eV.

UV–Vis measurements were performed using a UV–Vis-1601 Shimadzu spectrophotometer. Experimental uncertainty in wavelength lies within ±0.5 nm.

3. Results and discussion

The MALDI-TOF mass spectra of R_3PCo and R_4PCo (Fig. 1) show only a relevant peak at $m/z = 1240$ and 1408, respectively, for molecular ions detected as MH^+ species. These values strongly confirm both R_3PCo and R_4PCo structures.

Fig. 2 (black solid line) shows the UV–Vis spectrum of a 3.5×10^{-7} M THF solution of R_4PCo. Two features are evident: a Soret band at 419.7 nm and a broad band at 533.2 nm. The most evident difference between the present cobalt porphyrin UV–Vis spectrum and that of the free porphyrin [28] is represented by

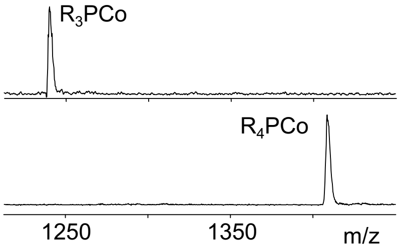

Fig. 1. The MALDI-TOF mass spectra of R_3PCo and R_4PCo.

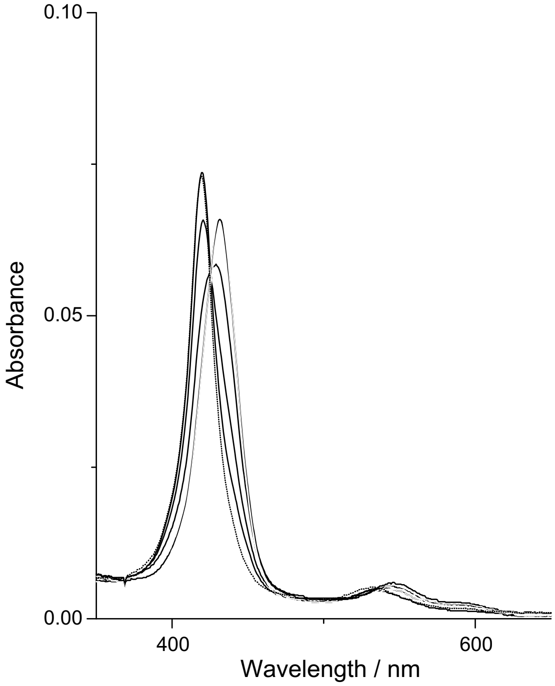

Fig. 2. UV–Vis spectra of a 3.5×10^{-7} M THF solution of the R_4PCo detected after 5, 10, 30, 60, 120 and 150 s bubbling 10 ppm NO_2 in N_2. The dashed line refers to the recovered starting spectrum.