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 $4\text{-ClCH}_2C_6H_4SiCl_3$ 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 Kα_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

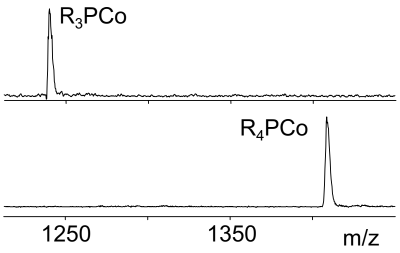

Fig. 1. The MALDI-TOF mass spectra of R_3PCo and R_4PCo.

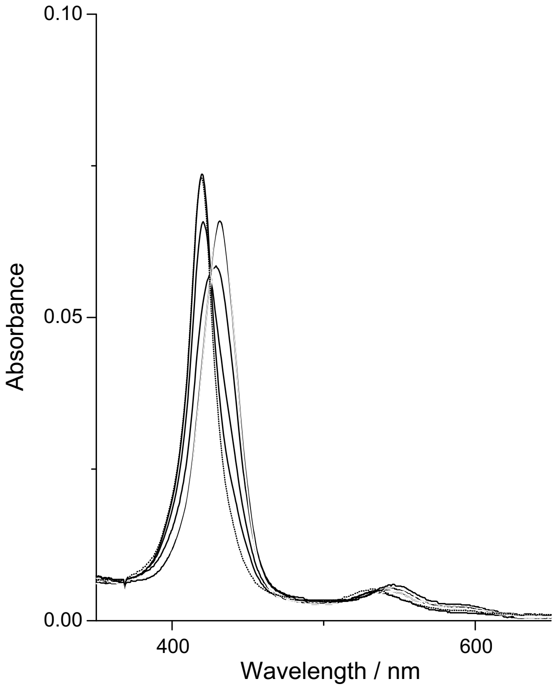

Fig. 2. UV–Vis spectra of a 3.5×10^{-7} M THF solution of the R_4PCo detected after 5, 10, 30, 60, 120 and 150 s bubbling 10 ppm NO_2 in N_2. The dashed line refers to the recovered starting spectrum.

the decreased number of Q-bands. In fact, the free porphyrin solution shows four Q-bands in the 515–660 nm range. The decreased Q-band number can be interpreted on the basis of the already reported the so-called four-orbital model that describes the low-lying (π,π^*) excited states of porphyrins in terms of electronic transitions between the two topmost filled molecular orbitals (HOMO's), a_{2u} (π) and a_{1u} (π), to two degenerate lowest empty molecular orbitals (LUMO's), e_g (π^*) [36]. On the basis of this model, metallo-porphyrins should show two visible Q-bands whilst, the free base shows four Q-bands. Taking into account all these observations, the broad envelope at 533.2 nm, observed for the present R_4PCo complex, accounts for two Q-bands [29c].

The NO_2 sensing capability of the present cobalt porphyrin system was first tested in solution. The UV–Vis spectra (Fig. 2) of the THF porphyrin 3.5×10^{-7} M solution, during bubbling of 10 ppm NO_2 in a N_2 gas stream (flow rates = 100 sccm), show an evident red shift of both Soret and Q-band that now appear at 432 and 548 nm, respectively. In particular, UV–Vis spectra were acquired after 5, 10, 30, 60, 120 and 150 s bubbling 10 ppm NO_2 in N_2. In addition, the Soret band suffers some intensity decrease whilst, the broad band at 548 nm shows an intensity increase and, as a consequence, the second Q-band at 591 nm it is now more evident. The starting spectrum was totally recovered by removing the solvent in vacuum and re-dissolving the solid in THF. This result confirms the reversible sensing capability of the present system towards NO_2 at ppm level. On the basis of this observation, a sensing mechanism consistent with cobalt coordination chemistry can be inferred.

The R_3PCo-SAM (Fig. 3) was synthesized by covalent grafting of the cobalt porphyrin to a silica substrate that was previously cleaned, hydroxylated and silylated. In particular, the silylation was performed rigorously under inert atmosphere, with the Cl_3–Si–C_6H_4–CH_2Cl siloxane, a bi-functional coupling agent that bonds both the substrate and the cobalt porphyrin molecules. This porphyrin siloxane-based monolayer strongly adhere to the substrate, is robust since insoluble in common organic solvents, and cannot be removed by the "Scotch-tape decohesion" test as evidenced by UV–Vis measurements. Comparison between the UV–Vis spectrum for R_3PCo-SAM (Fig. 4, solid line) and that of the R_4PCo complex in solution (Fig. 2) is straightforward once a 16 nm red shift for the monolayer is taken into account.

Using the Beer–Lambert law ($A = \varepsilon lc$, where A is the absorbance and ε, l and c are the extinction coefficient, the thickness and the density of the porphyrin in the layer, respectively), one can calculate the surface coverage, $d_{\text{surf}} = A\varepsilon^{-1}$ (number of cobalt porphyrin molecules/cm^2 of the R_3PCo-SAM) [37,38]. Taking into account the ε value of 210000 in THF, the calculated density value is 6.31×10^{12} molecules/cm^2. This value is lower than that already observed for the free porphyrin SAM (1.1×10^{13}) and can be understood in terms of increased interactions between porphyrin molecules due to the presence of Co(II) ions in the porphyrin core.

The molecular monolayer characterization of the R_3PCo-SAM was carried out with X-ray photoelectron spectroscopy. This technique is ideal since it allows high vertical resolution, gives information on the bonding states of the grafted molecules [22–31], and allows to estimate the surface elemental composition, making due allowance for the relevant atomic sensitivity factors [39].

In particular, the Si 2p, at 103.1 eV and the O 1s, at 533.2 eV signals are consistent with the presence of the SiO_2 substrate [40–42]. The C 1s spectrum with band at 285.0 and 286.5 eV is typical for porphyrin systems [43–47].

The cobalt porphyrin complex possesses a D_{4h} symmetry. Therefore, all nitrogen atoms are equivalent and should show a symmetric N 1s XPS peak. Indeed, this behavior has been reported for CuTPC and CuTPP porphyrin systems that show the N 1s signal at 398.3 and 398.2 eV, respectively [44]. In addition, a broad therefore uninformative N 1s band in the 402–395 eV range has been revealed for a zinc protoporphyrin monolayer linked to amino-terminated silanized glass surfaces [48]. Besides, some zinc porphyrin polymers display two N 1s peaks (∼400 eV) due to multiple chemical environments at the porphyrin nitrogen atoms that, in turn, cause different intermolecular interactions [43]. The N 1s spectrum of the present R_3PCo-SAM (Fig. 5) shows a peak at

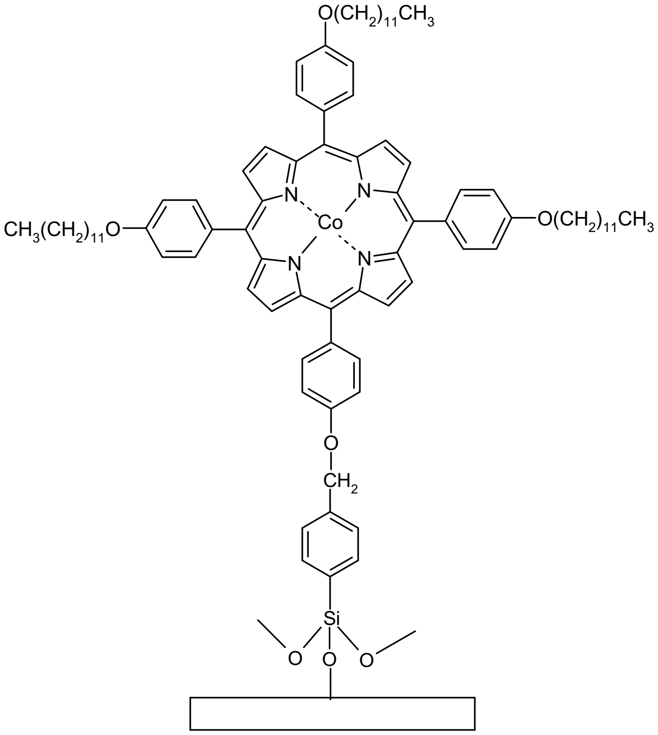

Fig. 3. R_3PCo-SAM.

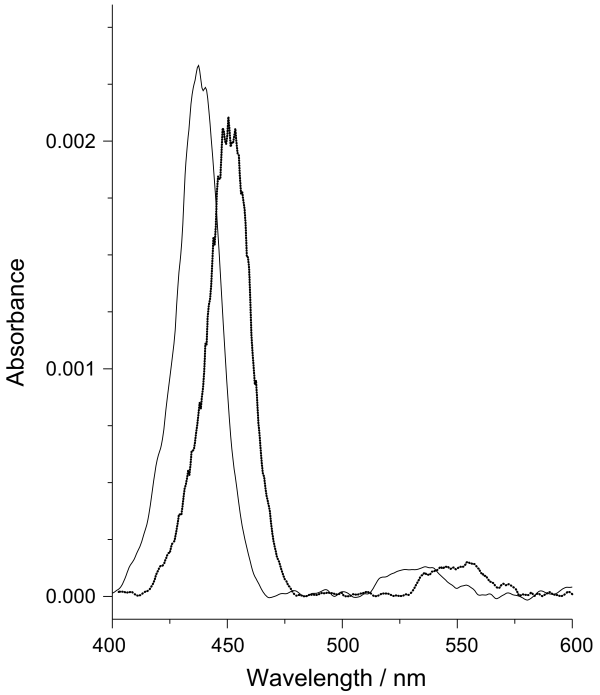

Fig. 4. UV–Vis spectra of a representative R_3PCo-SAM in air (solid line) and upon 10 ppm NO_2 in N_2 (dashed line).

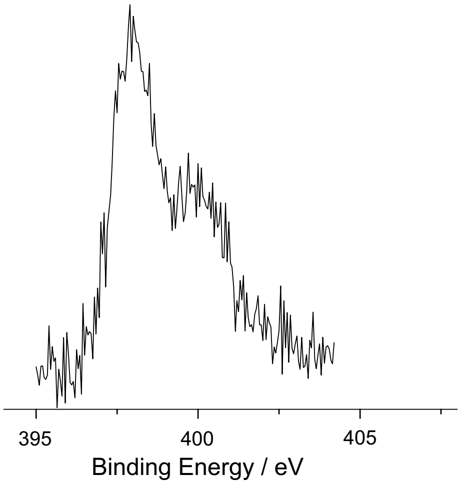

Fig. 5. XPS of the R_3PCo-SAM in the N 1s energy region.

398.0 eV with an intense shoulder at 400.1 eV [11,43,44,48–50]. According to these reported studies on similar porphyrin systems, the presence of the shoulder is consistent with the lift of the D_{4h} symmetry that, in turn, cause the lift of the nitrogen–cobalt interaction degeneracy because of the cobalt porphyrin axial ligation to the silylated substrate [43].

The XPS signal at 778.2 eV (Fig. 6) accounts for the Co $2p_{3/2}$ spin–orbit component thus confirming the presence of the R_3PCo on the surface. This value is almost coincident with already reported XPS data for parent systems [13a].

Further experiments were made to rule out either any possible physisorption or alternative Si–O–porphyrin surface grafting. A hydrophilic SiO_2 terminated surface was exposed to a 1×10^{-4} M R_3PCo solution and then rinsed. Neither UV–Vis nor XPS evidences of cobalt porphyrin were found.

It can be noticed that the coupling of UV–Vis and XPS techniques is very useful to study monolayers since provides chemical information that are unique and not available with many other spectroscopic techniques.

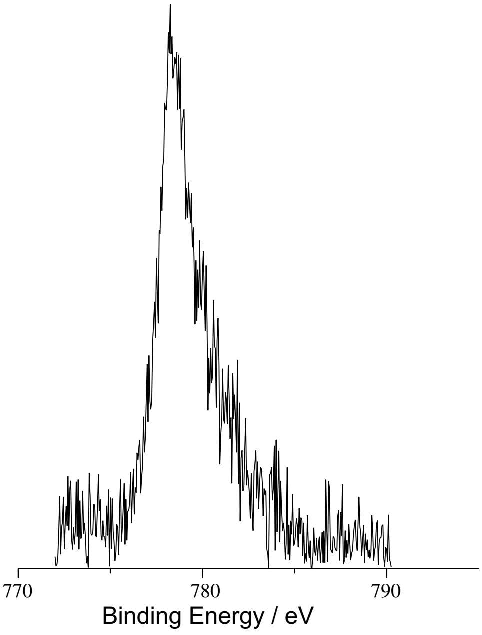

Fig. 6. XPS of the R_3PCo-SAM in the Co $2p_{3/2}$ energy region.

Finally, the NO_2 molecular recognition capability of the R_3PCo-SAM was investigated by UV–Vis measurements. In particular, the monolayer-bearing substrate was fixed in a cuvette sealed with a septa rubber lid. UV–Vis spectra were recorded before and upon 10 ppm NO_2 in N_2. Fig. 4 (dashed line) shows evidence of a ~15 nm higher wavelength shifted spectrum, in tune with the behavior already observed in the solution, thus confirming the ability of the system to detect NO_2.

4. Conclusions

In the present study, two new cobalt porphyrin systems have been obtained and their sensing characteristics towards NO_2 exploited. Therefore, a new monolayer of one of these cobalt porphyrin molecules, covalently assembled to a silylated substrate, was synthesized. This robust monolayer system was characterized using both UV–Vis and X-ray photoelectron measurements. A well-resolved XPS Co $2p_{3/2}$ signal confirms the cobalt porphyrin assembling. The absorbance spectrum of the monolayer closely resembles that of the R_4PCo solution and provides evidence of NO_2 molecular recognition ability. Further efforts concerning the selectivity towards NO_2 of the present R_3PCo-SAM are in progress. Since the ultimate goal of molecular bottom-up approaches is to employ functional building blocks to construct nanometer-scale devices that address specific applications, such a monolayer is a good candidate for the development of sensor, switches, displays and magnetic devices.

Acknowledgements

The authors thank the NATO (SfP project 981964) and the Ministero Universitaè Ricerca (MUR, Roma) for financial supports (PRIN 2005 and FIRB 2003).

References

[1] (a) N. Crivillers, M. Mas-Torrent, S. Perruchas, N. Roques, J. Vidal-Gancedo, J. Veciana, C. Rovira, L. Basabe-Desmonts, B.J. Ravoo, M. Crego-Calama, D.N. Reinhoudt, Angew. Chem., Int. Ed. 46 (2007) 2215;
(b) C. Altavilla, E. Ciliberto, A. Aiello, C. Sangregorio, D. Gatteschi, Chem. Mater. 19 (2007) 5980;
(c) F. Pineider, M. Mannini, R. Sessoli, A. Caneschi, D. Barreca, L. Armelao, A. Cornia, E. Tondello, D. Gatteschi, Langmuir 23 (2007) 11836;
(d) M. Mannini, L. Sorace, L. Gorini, F.M. Piras, A. Caneschi, A. Magnani, S. Menichetti, D. Gatteschi, Langmuir 23 (2007) 2389;
(e) M. Mannini, D. Bonacchi, L. Zobbi, F.M. Piras, E.A. Speets, A. Caneschi, A. Cornia, A. Magnani, B.J. Ravoo, D.N. Reinhoudt, R. Sessoli, D. Gatteschi, Nano Lett. 5 (2005) 1435;
(f) C. Altavilla, E. Ciliberto, D. Gatteschi, C. Sangregorio, Adv. Mater. 17 (2005) 1084;
(g) G.G. Condorelli, A. Motta, I.L. Fragalà, F. Giannazzo, V. Raineri, A. Caneschi, D. Gatteschi, Angew. Chem. 43 (2004) 4081;
(h) T. Osa, M. Fujihira, Nature 264 (1976) 349.
[2] M.-S. Chen, C.S. Dulcey, L.A. Chrisey, W.J. Dressick, Adv. Funct. Mater. 16 (2006) 774.
[3] W. Lin, G.K. Wong, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 8034.
[4] (a) Z. Liu, A.A. Yasseri, R.S. Loewe, A.B. Lysenko, V.L. Malinovskii, Q. Zhao, S. Surthi, Q. Li, V. Misra, J.S. Lindsey, D.F. Bocian, J. Org. Chem. 69 (2004) 5568;
(b) Z. Liu, A.A. Yasseri, J.S. Lindsey, D.F. Bocian, Science 302 (2003) 1543.
[5] H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, T.K. Ahn, S.K. Kim, D. Kim, S. Fukuzumi, J. Am. Chem. Soc. 1250 (2003) 9129.
[6] T. van der Boom, G. Evmenenko, P. Dutta, M.R. Wasielewski, Chem. Mater. 15 (2003) 4068.
[7] A. Facchetti, A. Abbotto, L. Beverina, M.E. van der Boom, P. Dutta, G. Evmenenko, G.A. Pagani, T.J. Marks, Chem. Mater. 15 (2003) 1064.
[8] P. Samori, V. Francke, V. Enkelmann, K. Muellen, J.P. Rabe, Chem. Mater. 15 (2003) 1032.
[9] J.H. Fendler, Chem. Mater. 13 (2001) 3196.
[10] P. Gomez-Romero, Adv. Mater. 13 (2001) 163.
[11] (a) D.A. Offord, S.B. Sachs, M.S. Ennis, T.A. Eberspacher, J.H. Griffin, C.E.D. Chidsey, J.P. Collman, J. Am. Chem. Soc. 120 (1998) 4478;
(b) D.Q. Li, B.I. Swanson, J.M. Robinson, M.A. Hoffbauer, J. Am. Chem. Soc. 115 (1993) 6975.

[12] (a) P.Y. Keng, I. Shim, B.D. Korth, J.F. Douglas, J. Pyun, ACS Nano 1 (2007) 279;
(b) K. Schulte, J.C. Swarbrick, N.A. Smith, F. Bondino, E. Magnano, Adv. Mater. 19 (2007) 3312;
(c) R. Lescouezec, J. Vaissermann, C. Ruiz-Perez, F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzee, D. Gatteschi, W. Wernsdorfer, Angew. Chem., In. Ed. 42 (2003) 1483;
(d) M.F. Casula, A. Corrias, A. Falqui, V. Serin, D. Gatteschi, C. Sangregorio, C. de Fernandez, G. Battaglin, Chem. Mater. 15 (2003) 2201;
(e) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G. Pini, M.A. Novak, Angew. Chem., Int. Ed. 40 (2001) 1760.

[13] (a) K. Flechtner, A. Kretschmann, H.-P. Steinrück, M. Gottfried, J. Am. Chem. Soc. 129 (2007) 12110;
(b) M. Lu, B. Chen, T. He, Y. Li, J.M. Tour, Chem. Mater. 19 (2007) 4447;
(c) I. Zilbermann, E. Maimon, R. Ydgar, A.I. Shames, E. Korin, L. Soifer, A. Bettelheim, Inorg. Chem. Commun. 7 (2004) 1238;
(d) Y. Wang, J. Kang, H. Wu, Z. Xue, X. Lu, Anal. Lett. 37 (2004) 575;
(e) R.S. Loewe, A. Ambroise, K. Muthukumaran, K. Padmaja, A.B. Lysenko, G. Mathur, Q. Li, D.F. Bocian, V. Misra, J. S Lindsey, J. Org. Chem. 69 (2004) 1453;
(f) S. Griveau, V. Albin, T. Pauporte, J.H. Zagal, F. Bedioui, J. Mater. Chem. 12 (2002) 225;
(g) S. Zou, R.S. Clegg, F.C. Anson, Langmuir 18 (2002) 3241.

[14] S. Berner, S. Biela, G. Ledung, A. Gogoll, J.-E. Baeckvall, C. Puglia, S. Oscarsson, J. Catal. 244 (2006) 86.

[15] S. Nardis, D. Monti, C. Di Natale, A. D'Amico, P. Siciliano, A. Forleo, M. Epifani, A. Taurino, R. Rella, R. Paolesse, Sens. Actuators B: Chem. B103 (2004) 339.

[16] (a) F. Armand, P.-A. Albouy, F. Da Cruz, M. Normand, V. Huc, E. Goron, Langmuir 17 (2001) 3431;
(b) V. Huc, F. Armand, J.P. Bourgoin, S. Palacin, Langmuir 17 (2001) 1928;
(c) G.A. Schick, I.C. Schreiman, R.W. Wagner, J.S. Lindsey, D.F. Bocian, J. Am. Chem. Soc. 111 (1989) 1344.

[17] (a) F. Armand, P.-A. Albouy, F. Da Cruz, M. Normand, V. Huc, E. Goron, Langmuir 17 (2001) 3431;
(b) L. Scudiero, D.E. Barlow, U. Mazur, K.W. Hipps, J. Am. Chem. Soc. 123 (2001) 4073.

[18] A.H. Ell, G. Csjernyik, V.F. Slagt, J.-E. Baeckvall, S. Berner, C. Puglia, G. Ledung, S. Oscarsson, Eur. J. Org. Chem. 5 (2006) 1193.

[19] V. Arima, E. Fabiano, R.I.R. Blyth, F. Della Sala, F. Matino, J. Thompson, R. Cingolani, R. Rinaldi, J. Am. Chem. Soc. 126 (2004) 16951.

[20] G. Kalyuzhny, A. Vaskevich, S. Matlis, I. Rubinstein, Rev. Anal. Chem. 18 (1999) 237.

[21] N. Micali, V. Villari, P. Mineo, D. Vitalini, E. Scamporrino, V. Crupi, D. Majolino, P. Migliardo, V. Venuti, J. Phys. Chem. B 107 (2003) 5095.

[22] A. Gulino, S. Giuffrida, P. Mineo, M. Purrazzo, E. Scamporrino, G. Ventimiglia, M.E. van der Boom, I. Fragalà, J. Phys Chem. B 110 (2006) 16781.

[23] A. Gulino, P. Mineo, E. Scamporrino, D. Vitalini, I. Fragalà, Chem. Mater. 18 (2006) 2404.

[24] A. Gulino, G.G. Condorelli, P. Mineo, I. Fragalà, Nanotechnology 16 (2005) 2170.

[25] A. Gulino, P. Mineo, S. Bazzano, D. Vitalini, I. Fragalà, Chem. Mater. 17 (2005) 4043.

[26] A. Gulino, S. Bazzano, G.G. Condorelli, S. Giuffrida, P. Mineo, C. Satriano, E. Scamporrino, G. Ventimiglia, D. Vitalini, I. Fragalà, Chem. Mater. 17 (2005) 1079.

[27] A. Gulino, S. Bazzano, P. Mineo, E. Scamporrino, D. Vitalini, I. Fragalà, Chem. Mater. 17 (2005) 521.

[28] A. Gulino, P. Mineo, E. Scamporrino, D. Vitalini, I. Fragalà, Chem. Mater. 16 (2004) 1838.

[29] (a) A. Gulino, P. Mineo, I. Fragalà, J. Phys. Chem. C 111 (2007) 1373;
(b) A. Gulino, F. Lupo, G.G. Condorelli, P. Mineo, I. Fragalà, Chem. Mater. 19 (2007) 5102;
(c) A. Gulino, E. Scamporrino, D. Vitalini, I. Fragalà, J. Phys. Chem. C 111 (2007) 14125.

[30] H. Cohen, O.V. Zenkina, A.D. Shukla, M.E. van der Boom, J. Phys. Chem. B 110 (2006) 1506.

[31] E. Frydman, H. Cohen, R. Maoz, J. Sagiv, Langmuir 13 (1997) 5089.

[32] (a) D. Vitalini, P. Mineo, E. Scamporrino, Macromolecules 32 (1999) 60;
(b) P. Mineo, E. Scamporrino, D. Vitalini, Macromol. Rapid Commun. 23 (2002) 681.

[33] A. Gulino, S. La Delfa, I. Fragalà, R.G. Egdell, Chem. Mater. 8 (1996) 1287.

[34] A. Gulino, G.G. Condorelli, I. Fragalà, R.G. Egdell, Appl. Surf. Sci. 90 (1995) 289.

[35] M. Repoux, Surf. Interf. Anal. 18 (1992) 567.

[36] (a) H. Ryeng, A. Ghosh, J. Am. Chem. Soc. 124 (2002) 8099;
(b) A.K. Wertsching, A.S. Koch, S.G. Di Magno, J. Am. Chem. Soc. 123 (2001) 3932;
(c) A.B.J. Parusel, A. Ghosh, J. Phys. Chem. A 104 (2000) 2504;
(d) T. Hashimoto, Y.-K. Choe, H. Nakano, K. Hirao, J. Phys. Chem. A 103 (1999) 1894;
(e) J.A. Shelnutt, V. Ortiz, J. Phys. Chem. 89 (1985) 4733;
(f) M.-Y.R. Wang, B.M. Hoffman, J. Am. Chem. Soc. 106 (1984) 4235;
(g) P.J. Spellane, M. Gouterman, A. Antigas, S. Kim, Y.C. Liu, Inorg. Chem. 19 (1980) 386;
(h) M. Goutermann, in: D. Dolphin (Ed.), The Porphyrins, Academic press, New York, 1978 (Chapter 3);
(i) D. Spangler, G.M. Maggiora, L.L. Shipman, R.E. Christoffersen, J. Am. Chem. Soc. 99 (1977) 7470.

[37] D.Q. Li, B.I. Swanson, J.M. Robinson, M.A. Hoffbauer, J. Am. Chem. Soc. 115 (1993) 6975.

[38] R. Yerushalmi, A. Scherz, M.E. van der Boom, J. Am. Chem. Soc. 126 (2004) 2700.

[39] D. Briggs, 2nd ed., in: D. Briggs, M.P. Seah (Eds.), Practical Surfaces Analysis, vol. 1, Wiley-VCH Weinheim, Germany, 1995. p. 244.

[40] M.C. Capel-Sanchez, L. Barrio, J.M. Campos-Martin, J.L.G. Fierro, J. Coll. Interf. Sci. 277 (2004) 146.

[41] M.R. Alexander, R.D. Short, F.R. Jones, W. Michaeli, C. Blomfield, J. Appl. Surf. Sci. 137 (1999) 179.

[42] P. Taranekar, X. Fan, R. Advincula, Langmuir 18 (2002) 7943.

[43] D.M. Sarno, L.J. Matienzo, W.E. Jones Jr., Inorg. Chem. 40 (2001) 6308.

[44] D.H. Karweik, N. Winograd, Inorg. Chem. 15 (1976) 2336.

[45] B. Bartlett, J.M. Valdisera, J.N. Russell Jr., Surf. Sci. 442 (1999) 265.

[46] J.G. Serafin, C.M. Friend, J. Am. Chem. Soc. 111 (1989) 4233.

[47] G. Beamson, D. Briggs, Mol. Phys. 76 (1992) 919.

[48] Z. Zhang, R. Hu, Z. Liu, Langmuir 16 (2000) 1158.

[49] M.V. Zeller, R.G. Hayes, J. Am. Chem. Soc. 95 (1973) 3855.

[50] H. Yamashige, S. Matsuo, T. Kurisaki, R.C. Perera, H. Wakita, Anal. Sci. 21 (2005) 635.