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Communication

Pyridyl-substituted porphyrins on palladium nanoparticles

Thomas Mayer-Gall, Alexander Birkner, Gerald Dyker *

Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany

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Abstract

The influence of tetrapyridylporphyrins on agglomeration and solubility of palladium nanoparticles is tested. The comparison between 3-pyridyl- and 4-pyridyl-substituted porphyrins enables to distinguish between central and peripheric binding mode.

Keywords: Porphyrins; Nanoparticles; Surface chemistry; Aggregation; Palladium

1. Introduction

Porphyrins are of exceptional importance in nature, science and technology: for instance as ligands in transition metal catalysis, as photo-sensitizers and as building blocks for electronic devices [1]. Their electrochemical and photochemical activity should have a profound influence on the properties of metallic nanoparticles in corresponding heterosupramolecular assemblies [2]. Moreover, in the sense of "size matters" nano-scaled surfactants such as functionalized tetrakisarylporphyrins [3] – with a diameter of at least 1.5 nm and in connection with multiple binding sites – should in addition exhibit a strong influence on the formation as well as the aggregation of metallic nanoparticles [4].

In most studies concerning the interaction of porphyrins with metallic nanoparticles thio-functionalities are applied as anchor groups [5]. The tetra-4-pyridyl-substituted porphyrin **2** was shown to cross-link gold nanoparticles, thus stabilizing two-dimensional hexagonally packed arrays [6]. Especially with silver nanoparticles tetraphenylporphyrin was found to coordinate via the pyrrol nitrogens (proven by Raman spectroscopy), whereas gold nanoparticles seem to be inert towards this mode of bonding [7]. Herein we report on our results on the influence of pyridyl-substituted porphyrins **1** and **2** (Scheme 1) on the solubility of palladium nanoparticles with respect to the competing coordination sites: central pyrrol nitrogens versus peripheric pyridyl nitrogens.

2. Results and discussion

For the syntheses of palladium nanoparticles we chose the reduction of palladium acetate in propylene carbonate at 100 °C in accordance to the procedure of Reetz et al. [8,9], which generally delivers rather monodisperse particles in the range of 8–10 nm. The molar porphyrin/palladium ratio applied was about 1:40, whereas a ratio of 1:100 is estimated to be sufficient to completely cover a 4 nm palladium particle with centrally coordinated porphyrins.

A comparison of the properties of Pd-nanoparticles coated with 3-pyridyl- and 4-pyridyl-substituted porphyrins **1** and **2**, respectively, revealed tremendous differences: **1**@Pd-nanoparticles are insoluble in chloroform and methanol, but very well soluble in ethyl acetate. In contrast, freshly prepared **2**@Pd-nanoparticles are insoluble in chloroform and ethyl acetate, highly agglomerated according to TEM, but nevertheless soluble in methanol (see Fig. 1).

The IR spectra prove that the porphyrins are indeed enriched on the surface of the particles. Since the typical N–H valence signals are missing in the case of **1**@Pd-nanoparticles, a coordination at the central pyrrol nitrogens is assumed.

* Corresponding author. Tel.: +49 (0) 234 32 24551.
E-mail address: gerald.dyker@ruhr-uni-bochum.de (G. Dyker).

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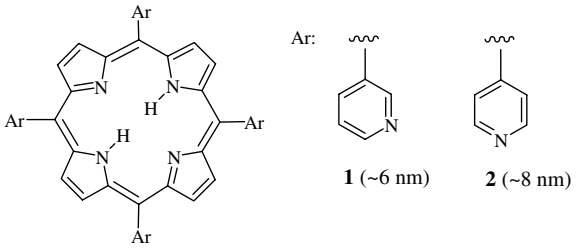

Scheme 1. Porphyrins tested in the synthesis of Pd-nanoparticles (average size is given in brackets).

Most importantly, the IR spectrum of **2**@Pd-nanoparticles – measured in nujol to avoid water signals – exhibits a small but significant N–H valence signal at 3447 cm^{-1} (IR spectrum A in Fig. 2), even after washing four times with acetone and with THF, clearly dissolving all porphyrin molecules, which were not bound to the nanoparticles. This signal finally disappears upon washing the nanoparticles with chloroform (IR spectrum B in Fig. 2) until the supernatant remains colourless. Moreover, also the solubility of **2**@Pd-nanoparticles changes dramatically with the chloroform washing process. They become soluble in ethyl acetate and insoluble in methanol, thus exhibiting essentially the same solubility as their **1**@Pd-counterparts. Tetraphenylporphyrin, tested as reference compound, also coordinates to the surface of the Pd-nanoparticles, significantly increasing both solubility and stability in chloroform as well as in THF (compared to Pd-nanoparticles in the absence of porphyrins). Also in this case the N–H valence signals are missing in the IR spectrum (in analogy to **1**@Pd-nanoparticles).

Our mechanistic interpretation explains the observed properties: in the case of the 3-pyridyl-substituted porphyrins **1** the kinetically favoured precoordination at the pyridyl groups is replaced by the thermodynamically favoured binding at the central pyrrol nitrogens (coating type A in Fig. 3), resulting in a relatively unpolar surface with no directly exposed functional groups. In the case of the 4-pyridyl-substituted porphyrins **2** we assume coating type B with mixed binding modes: gaps between the pyrrol-coordinated porphyrins are occupied with pyridine-coordinated porphyrins, perpendicular to the nanoparticle surface. As a consequence, the *trans*-pyridyl unit is in an exposed position, effecting both the agglomeration through cross-linking and the solubility in methanol through hydrogen bonds.

Washing off the pyridyl-bonded porphyrins with chloroform means changing the coating type from B to A, accompanied by the corresponding change in solubility.

In summary, we have developed a structural model of pyridylporphyrin-coated Pd-nanoparticles based on solubility, IR- and TEM-observations. Currently we are synthesizing flexible porphyrin arrays as ''molecular baseball gloves'': a single porphyrin array should be capable of completely wrapping a suitable metallic nanoparticle.

3. Experimental

For the preparation of the palladium nanoparticles a mixture of 22.4 mg (1.0 μmol) of palladium acetate and 40 μmol of the porphyrins **1** and **2** in 5 ml of propylene carbonate in a screw-capped tube with magnetic stirbar was placed in a preheated oil bath at 100 °C for 3 h. The reaction mixture was poured into a centrifuge tube and was diluted with 20 ml of an appropriate solvent, in which the nanoparticles were insoluble (methanol in the case of **1** and acetone in the case of **2**). After the first centrifugation the supernatant was removed and the nanoparticles were dissolved in a second solvent (ethyl acetate in the case of **1** and methanol in the case of **2**), to be again precipitated with the second solvent. After centrifugation the precipitate was washed under sonication with a third solvent, in which the porphyrins were soluble and the nanoparticles far less soluble (again acetone in the case of **1** and **2**; chloroform partially dissolves **2**, which is bound to the nanoparticle surface). The process of solubilization, precipitation and washing was repeated 3–6 times until no more porphyrins went into solution. Finally the nanoparticles were solubilized in 10 ml of the second solvent (**1** in ethyl

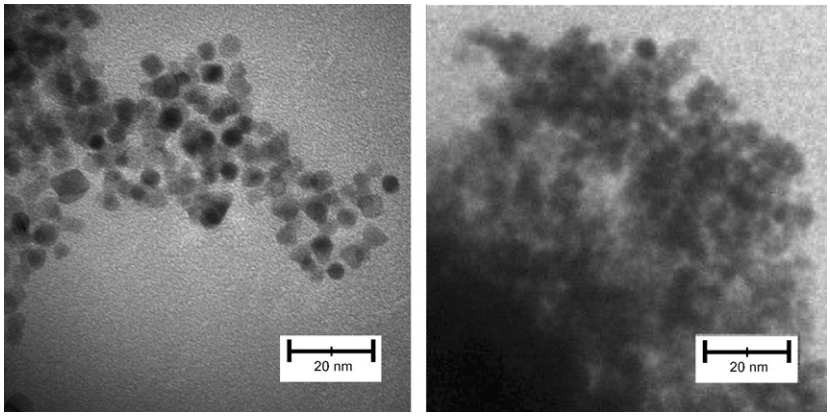

Fig. 1. TEM-images of the Pd-nanoparticles, left: coated with 3-pyridyl-substituted porphyrin **1**; right: highly agglomerated particles coated with 4-pyridyl-substituted porphyrin **2**.

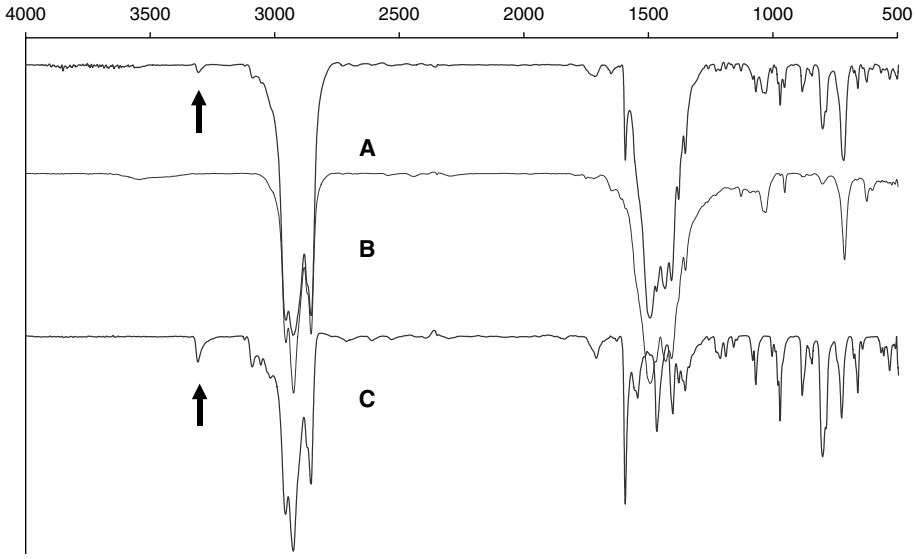

Fig. 2. Comparison of IR-difference spectra (minus nujol), focused on the N–H valence signal of tetrakis-4-pyridylporphyrin **2** (see arrows); spectrum A: **2**@Pd-nanoparticles after washing with acetone and methanol (but not chloroform!); spectrum B: **2**@Pd-nanoparticles after washing with chloroform; spectrum C: IR of porphyrin **2**.

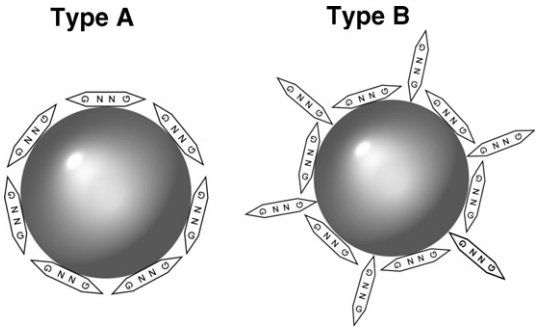

Fig. 3. Types of coating of Pd-nanoparticles with functionalized porphyrins; type A: coordination at central pyrrol-N's, type B: mixed situation with additional coordination at peripheric functional groups G.

acetate, **2** in methanol) to be distributed on carbon-coated copper grids.

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References

[1] (a) B. Meunier, Chem. Rev. 92 (1992) 1411;
(b) J.A.A.W. Elemans, R. van Hameren, R.J.M. Nolte, A.E. Rowan, Adv. Mater. 18 (2006) 1251;
(c) D. Holten, D.F. Bocian, J.S. Lindsey, Acc. Chem. Res. 35 (2002) 57;
(d) J.P. Collman, R. Boulatov, C.J. Sunderland, L. Fu, Chem. Rev. 104 (2004) 561;
(e) D.M. Guldi, G.M.A. Rahman, V.P. Sgobba, C. Ehli, Chem. Soc. Rev. 35 (2006) 471.
[2] D. Ryan, S.N. Rao, H. Rensmo, D. Fitzmaurice, J.A. Preece, S. Wenger, J.F. Stoddart, N. Zaccheroni, J. Am. Chem. Soc. 122 (2000) 6252, and references cited therein.
[3] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Am. Chem. Soc. 32 (1966) 476.
[4] For calixarenes, resorcinarenes and cyclodextrins as macrocyclic ligands for metallic, nanoparticles see (a) J. Liu, W. Ong, A.E. Kaifer, C. Peinador, Langmuir 18 (2002) 5981;
(b) A. Wei, Chem. Commun. (2006) 1581;
(c) M.S. Vickers, J. Cookson, P.D. Beer, P.T. Bishop, B. Thiebaut, J. Mater. Chem. 16 (2006) 209.
[5] (a) M. Yamada, A. Kuzume, M. Kurihara, K. Kubo, H. Nishihara, Chem. Commun. (2001) 2476;
(b) G. Li, J.H. Fuhrhop, Langmuir 18 (2002) 7740;
(c) A.H. Éll, G. Csjernyik, V.F. Slagt, J.-E. Bäckvall, S. Berner, C. Puglia, G. Ledung, S. Oscarsson, Eur. J. Org. Chem. (2006) 1193;
(d) G. Fantuzzi, P. Pengo, R. Gomila, P. Ballester, C.A. Hunter, L. Pasquato, P. Scrimin, Chem. Commun. (2003) 1004;
(e) T. Hasobe, H. Imahori, P.V. Kamat, T.K. Ahn, S.K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, J. Am. Chem. Soc. 127 (2005) 1216;
(f) H. Imahori, Y. Kashiwagi, T. Hanada, Y. Endo, Y. Nishimura, I. Yamazaki, S. Fukuzumi, J. Mater. Chem. 13 (2003) 2890;
(g) M. Kanehara, T. Teranishi, e-J. Surf. Sci. Nanotech. 3 (2005) 30.
[6] I. Sloufova-Smova, B. Vlckova, Nanoletter 2 (2002) 121.
[7] (a) K. Solecka-Cermakova, B. Vlckova, F. Lednicky, J. Phys. Chem. 100 (1996) 4954;
(b) B. Vlckova, P. Matejka, J. Simonova, K. Carmakova, P. Pancoska, V. Baumruk, J. Phys. Chem. 97 (1993) 9719.
[8] M.T. Reetz, G. Lohmer, Chem. Commun. (1996) 1921.
[9] For the influence of organic ligands on Pd nanoparticles, see E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gomez, A.M. Masdeu-Bulto, B. Chaudret, J. Organomet. Chem. 689 (2004) 4601–4610.