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Evidence that gold(III) porphyrins are *not* electrochemically inert: facile generation of gold(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin

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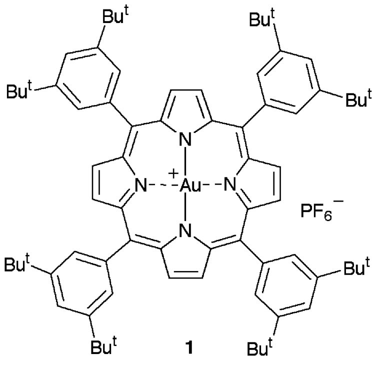
Gold(III) porphyrin 1 is shown to undergo reduction at the central metal ion to give the first known gold(II) porphyrin overturning the long held assumption that reduction of such complexes only occurs at the macrocycle.

Gold(III) porphyrins have been used as acceptors in porphyrin dyads[1,2] and triads[3] due to their ability to be easily reduced, either chemically or photochemically. The products of the first and second one-electron reductions are extremely stable in nonaqueous media but the singly reduced complexes can be chemically converted to a phlorin after disproportionation or further reduction in the presence of a proton source.[4] Early electrochemical experiments on (TPP)Au[$AuCl_4$] and two other gold porphyrins in DMSO showed the compounds to undergo three one-electron reductions[5] but the authors concluded, on the basis of electrochemical criteria and spectroelectrochemical data, that Au(III) was electrochemically inert when incorporated into a porphyrin macrocycle. This was also the conclusion based on theoretical calculations and electrochemical experiments involving the reduction of (TPP)AuCl in dichloromethane[6] and has since been assumed to be true for all other subsequently investigated gold(III) complexes.[7]

The first and second reversible half-wave potentials for reduction of gold porphyrins in functionalised multiporphyrin systems have sometimes been reported[1,3,8] but little attention has been paid to a third reduction or to the site of electron transfer itself which was invariably assumed but not proven to involve the porphyrin macrocycle. This is discussed in the present communication in which we report on the electrochemistry and spectral characterisations (UV-visible and ESR) of neutral and reduced hexafluorophosphate[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]gold(III), represented as (P)$AuPF_6$ **1**. Our studies were carried out in a variety of nonaqueous solvents and show that gold(III) porphyrins are not electrochemically inert as was previously claimed but can be rapidly and reversibly converted to a Au(II) form of the compound rather than to a Au(III) porphyrin π-anion radical.



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Three reversible one-electron reductions are seen for (P)$AuPF_6$ **1** in a variety of nonaqueous solvents including pyridine ($E_{1/2}$ = −0.52, −1.08 and −1.76 V), THF ($E_{1/2}$ = −0.40, −1.10 and −1.77 V) and benzonitrile ($E_{1/2}$ = −0.56, −1.09 and −1.81 V *vs.* SCE). The first electrode reaction involves the central metal ion and the next two, the conjugated porphyrin macrocycle. Evidence for assignment of a Au(III)/Au(II) process in the first reduction is given on the basis of electrochemistry coupled with UV-visible and ESR spectroscopy.

Cyclic voltammograms of (P)$AuPF_6$ **1** and (P)Cu^{II} in benzonitrile are illustrated in Fig. 1 while UV-visible spectra obtained upon reduction of the two compounds in a thin-layer cell are shown in Fig. 2. Two one-electron reductions are expected and observed for [5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II), (P)Cu^{II}, consistent with the stepwise formation of a porphyrin π-anion radical and dianion. In contrast, three reversible one-electron reductions are seen for (P)$AuPF_6$ **1** and indicate that one of the three processes must involve the central metal ion. As shown below, this reaction occurs prior to formation of a Au(II) porphyrin π-anion radical and dianion at more negative potentials.

Virtually identical UV-visible spectra are seen for the first reduction product of (P)$AuPF_6$ **1** (λ_{max} = 423 and 537 nm) and neutral (P)Cu^{II} (λ_{max} = 422 and 543 nm). Identical spectroelectrochemical results are also seen upon the second reduction of (P)$AuPF_6$ **1** and the first reduction of (P)Cu^{II} to its porphyrin π-anion radical form (see Fig. 2b and c). Similar spectral changes are seen in pyridine and dichloromethane and provide unequivocal evidence for the site of electron transfer in (P)$AuPF_6$ **1**.

Singly reduced (P)$AuPF_6$ **1** is characteristic of a neutral (P)M^{II} complex rather than a porphyrin π-anion radical. Its UV-visible spectrum in DMF, pyridine, dichloromethane or benzo-

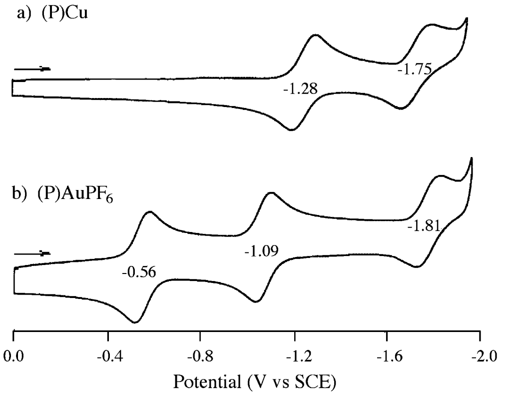

Fig. 1 Cyclic voltammograms of (a) (P)Cu^{II} and (b) (P)$AuPF_6$ **1** in benzonitrile containing 0.1 M TBAP.

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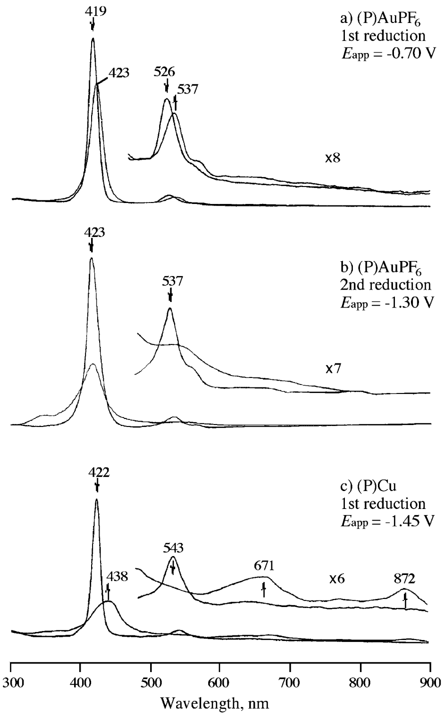

Fig. 2 Thin-layer UV-visible spectra before and after reduction of (P)AuPF$_6$ **1** and (P)Cu^{II} in benzonitrile containing 0.2 M TBAP.

nitrile has a well-defined Soret band at 420–423 nm and one major visible band at 534–537 nm. Similar shaped UV-visible spectra are also seen for other M(II) complexes having the same *tert*-butyl macrocycle, with three examples being given for (P)Zn^{II} (λ_{max} 430 and 560 nm), (P)Ni^{II} (λ_{max} 421 and 531 nm) and (P)Pd^{II} (λ_{max} 422 and 526 nm) in benzonitrile containing 0.1 M TBAP.[9]

The formation of a Au(II) species rather than a Au(III) porphyrin π-anion radical upon reduction was also confirmed by ESR spectra obtained after the chemical reduction of (P)AuPF$_6$ **1** with one equivalent of naphthalene radical anion in DMSO,[10] pyridine or benzonitrile.[11] These spectra are shown in Fig. 3.

The broad signal at g = 2.06 is quite different from the sharp signal at g = 2.006 which is assigned to the Au(III) porphyrin π-anion radical.[12] The large g-value (2.06), which is characteristic of the metal-centred radical, agrees with the reported value (2.065 ± 0.005) of Au(II) phthalocyanine.[13] A hyperfine interaction with ^{197}Au (I = 3/2, A = 27 G) is observed in benzonitrile.[14] Thus, the broad signal is clearly assigned to the Au(II) species. Although both the Au(II) porphyrin and the Au(III) porphyrin π-anion radical are evident in the frozen solution, the latter species is negligible judging from the large difference in their linewidths.[15] The initial formation of a transient porphyrin π-anion radical prior to the conversion to a stable Au(II) derivative cannot be ruled out. This point needs to be thoroughly investigated in the case of donor–acceptor complexes containing gold porphyrins where the site of reduction may vary with minor changes in the macrocycle, solvent or associated counterions and may thus have strong implications in interpretation of the photophysical data. In particular, reduction of a Au(III) porphyrin complex to a Au(II) porphyrin will result in loss of the associated ligand/counterion which might impede back electron transfer, as might interconversion between a Au(II) porphyrin and Au(III) porphyrin π-anion radical forms.

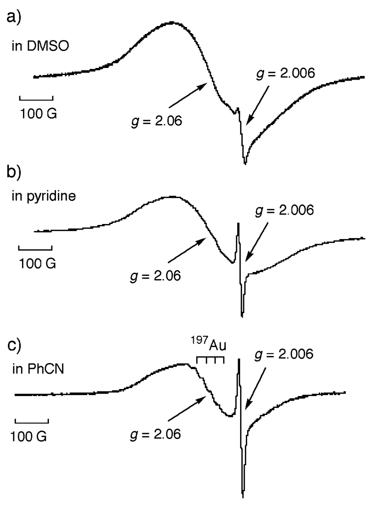

Fig. 3 ESR spectra of singly reduced (P)AuPF$_6$ **1** (1.0 mM) generated by the reduction with one equivalent of naphthalene radical anion (1.0 mM) in deaerated (a) DMSO, (b) pyridine and (c) benzonitrile at −160 °C.

In summary, the UV-visible, electrochemical and ESR data are self-consistent and clearly indicate that the investigated Au(III) porphyrin undergoes an initial metal-centred reduction followed by formation of a porphyrin π-anion radical and dianion at more negative potentials. Ongoing studies in our laboratories suggest that this is a general phenomenon for a wide range of gold(III) porphyrins.

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10 In DMSO, the generated Au(II) species becomes insoluble. This resulted in disappearance of the Soret band which had been used as criteria for formation of the π-anion radical in the case of a related [(TPP)Au]$^+$ complex.[5]
11 The reduction of **1** can also be achieved using tetramethylsemiquinone anion radical in benzonitrile. The electron transfer rate was too fast to be followed spectrometrically.
12 Only the isotropic g-value was determined because of the apparent isotropic signal due to the broad linewidth. The broad signal has precluded determination of the coordination symmetry.
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14 The A value is larger than the corresponding value of Au(II) phthalocyanine (A = 22 G) but smaller than the value of solvated Au^{2+} ion (A = 48 G). This indicates that the spin density is partially delocalized on the ligand. See: F. G. Herring, G. Hwang, K. C. Lee, F. Mistry, P. S. Phillips, H. Willner and F. Aubke, *J. Am. Chem. Soc.*, 1992, **114**, 1271.
15 Although only the ESR signal due to the π-anion radical is observable in solution at 25 °C because of the fast relaxation time of the Au(II) species, the amount of the π-anion radical is still negligible as compared to the initial concentration of (P)AuPF$_6$ **1**.