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Zinc metalloporphyrin-functionalised nanoparticle anion sensors†

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Disulfide-functionalised zinc metalloporphyrins self-assembled on gold nanoparticles exhibit remarkable, surface-enhanced, anion binding affinities as compared to the free metalloporphyrin.

The combined processes of molecular-scale recognition and surface assembly offer a powerful route to the development of refined sensing systems and, more generally, new technological devices based on controlling and analysing interactions on the nanometre scale. The design and construction of receptors which can selectively recognise and sense anionic guest species *via* a macroscopic physical response is a current area of chemical sensor technology receiving considerable attention.[1–3] We have recently developed methods whereby redox-active anion receptors can be assembled on planar gold electrodes in the formation of highly-selective sensors.[4]

Metal nanoparticles have extraordinary size-dependent optical properties, not present in the bulk metal and have, consequently, been the subject of intense research during the past decade or so.[5] Specifically, nanoparticles of silver, gold and copper show distinct and well-defined plasmon absorption in the visible spectrum, an absorption characterised by an extremely large molar absorption coefficient.[6] Attention has recently focused on functionalizing colloidal nanoparticles with molecular recognition components for potential sensing applications.[5,7]

With the ultimate aim of producing optical and redox-active nanoparticle anion sensors, we report here the synthesis of a new amide-disulfide functionalised zinc metalloporphyrin.[8] This compound was self-assembled on to gold nanoparticles to produce a novel anion-selective optical sensing system (Fig. 1). Importantly, surface pre-organisation of the neutral zinc metalloporphyrin moiety significantly enhances anion coordination at the nanoparticle surface to such an extent that recognition in a mixed aqueous–organic solvent system is possible.

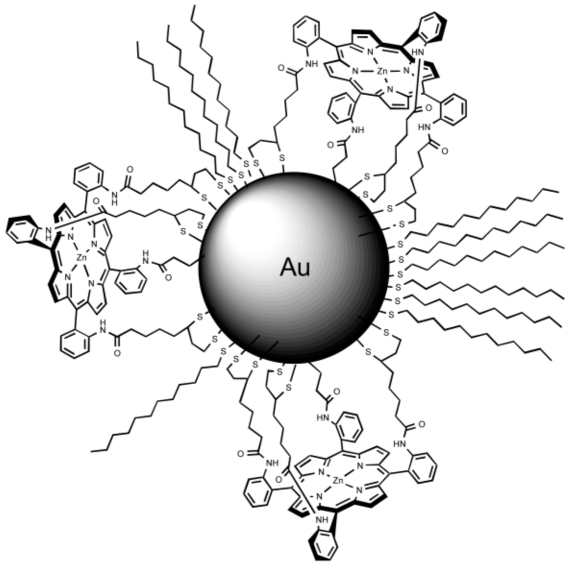
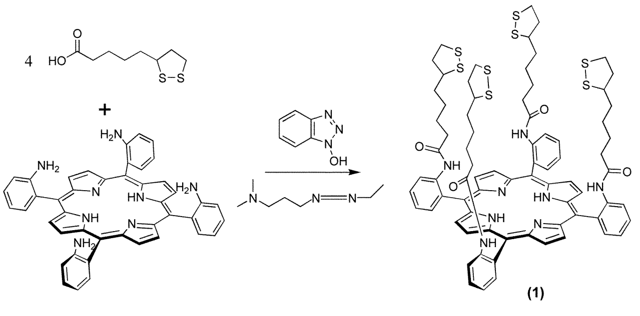


Fig. 1 Schematic of the anion-sensing porphyrin gold nanoparticle **3**.

The amide-disulfide functionalised porphyin **1** was prepared in 37% yield from the condensation reaction of the α,α,α,α-atropisomer of 5,10,15,20-*meso*-tetrakis(*o*-aminophenyl)porphyrin[9] and four equivalents of thioctic acid in the presence of DCCI and HOBt (Scheme 1). Reaction of **1** with Zn(OAc)$_2$ produced the metalloporphyrin derivative **2** in 75% yield. Gold nanoparticles were synthesized *via* the Brust method,[10] using dodecanethiol as the protecting thiol. Porphyrin-modified nanoparticles **3** were subsequently obtained by ligand substitution. Briefly, this was achieved by the addition of **2** to a chloroform solution of gold nanoparticles, stirring for 20 hours, solvent removal, then recrystallisation from chloroform and diethyl ether. Non-covalently bound **2** was removed by washing the resulting solid exhaustively with methanol and acetone until the liquor ran colourless. Modified nanoparticles were characterized by ^{1}H and ^{13}C NMR, UV-Vis. spectroscopy, elemental analysis, mass spectroscopy and thin layer chromatography.[11] The number of porphyrin receptor moieties per nanoparticle was estimated, using TEM-derived nanoparticle diameters, an estimate of the receptor "footprint" and elemental analysis, to be 30–80 (depending on particle size 3–4 nm).

Comparative UV-Visible titrations of **2** and **3** with a variety of anions in dichloromethane solution were undertaken by monitoring the porphyrin chromophore characteristics (Fig. 2). The association constants for 1 : 1 complexes were then calculated using the Specfit program.[12] The anion is, presumably, bound by a combination of



Scheme 1 Synthesis of the amide-disulfide porphyrin.

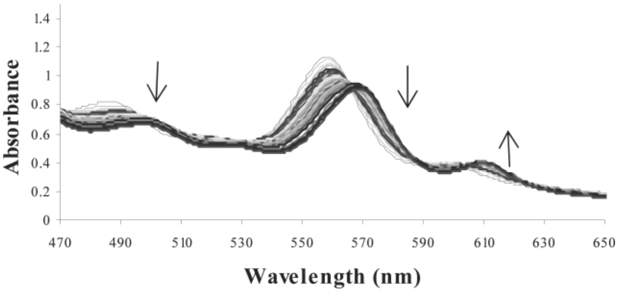


Fig. 2 Titration of a 50 μM solution of **3** with [TBA] [Br] in dichloromethane. Note: the nanoparticle plasmon band lies below the metalloporphyrin chromophore absorption.

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† Electronic supplementary information (ESI) available: synthetic procedure for **1** and **2**, titration experimental protocol and nanoparticle TEM. See http://www.rsc.org/suppdata/cc/b3/b313658b/

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interactions with the zinc Lewis acid centre and favourable anion–amide hydrogen bonding effects. The data obtained in dichloromethane solution (Table 1) are indicative of extremely strong complex formation between **2** and **3** with both Cl^- and $H_2PO_4^-$. The relative binding affinities are consistent with a trend expected on the basis of relative anion basicities. Table 1 also displays the striking result that the porphyrin-functionalised nanoparticle **3** exhibits significantly larger magnitudes of association constant, in comparison to **2**, for Br^-, I^- and NO_3^-.[13] This observation is further reinforced by the results of anion complexation studies carried out in the competitive solvent DMSO (Table 2). Particularly striking are the respective chloride binding affinities, where the surface-confined porphyrin-functionalised nanoparticle species **3** binds chloride more than two orders of magnitude more strongly than the zinc metalloporphyrin **2**. A remarkable enhancement in anion complex stability is also seen with dihydrogen phosphate and **3**. Analogous UV-Vis. titration experiments in 90% DMSO–10% water solvent mixtures revealed that neutral **3** is even capable of sensing Cl^- and $H_2PO_4^-$ in this aqueous solvent medium, though Specfit was unable to quantitatively analyse the titration data.[14]

This increase in association constant for anion recognition observed on confining the receptor to a surface is significant.[15] Host–guest binding affinity is determined by factors controlling enthalpy and entropy. By “pre-organising” receptors on surfaces, and thereby reducing their conformational flexibility (a contribution which increases the energetic cost of association), entropic contributions would be expected to be more favourable. Solvation effects associated with close packing of receptors in a dominantly hydrophobic self-assembled monolayer environment are also likely to be significant.

In summary, zinc metalloporphyrins self-assembled on gold nanoparticles exhibit remarkable enhanced anion binding affinities with respect to that of the free metalloporphyrin. The surface pre-organisation of optical and/or electrochemical-group functionalised host systems offers the opportunity to fabricate highly-sensitive sensory devices.

Table 1 Association constant (log *K*) data for **2** and **3** in dichloromethane determined at 293 K, errors ±0.1

Anion	**2**	**3**[a]
Cl^-	> 6	> 6
Br^-	4.1	5.0
I^-	3.2	4.0
NO_3^-	2.4	3.2
$H_2PO_4^-$	> 6	> 6
ClO_4^-	0	0

[a] Association constant values for the 1 : 1 porphyrin–anion complex on the nanoparticle surface.

Table 2 Association constant (log *K*) data of **2** and **3** in DMSO determined at 293 K, errors ±0.1

Anion	**2**	**3**[a]
Cl^-	< 2	4.3
$H_2PO_4^-$	2.5	4.1

[a] Association constant values for the 1 : 1 porphyrin–anion complex on the nanoparticle surface.

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13 Control experiments confirmed that the presence of mM levels of anions had a negligible effect on the UV-Vis. characteristics of dodecanethiol-stabilised gold nanoparticles.
14 As expected with moieties confined to the surface of gold nanoparticles, ^1H and ^{13}C NMR spectra of **3** are broad; this precludes the possibility of carrying out reliable NMR anion titration experiments.
15 In a recent study Labande *et al.* (reference 7) utilized hydrogen-bonding amidoferrocene dendritic receptors on gold nanoparticles for voltammetric anion sensing where enhanced anion binding was referred to as a “positive dendritic effect”.