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Detection of ppm quantities of gaseous SO$_2$ by organoplatinum dendritic sites immobilised on a quartz microbalance†

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Sensor devices for the detection of low quantities of SO$_2$ gas have been constructed which comprise organoplatinum receptor sites for the selective recognition of SO$_2$ and a quartz crystal microbalance for the detection of small mass changes at the receptor sites.

The development of efficient sensor materials on a chemical level relies on the selective binding of a substrate by well-defined molecular recognition sites. Organoplatinum complexes containing the monoanionic *N,C,N*-terdentate coordinating pincer[1] ligand [C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4]$^-$ have been shown to provide organometallic receptor sites for the reversible binding of sulfur dioxide (SO$_2$).[2] Recently, the heterogeneous working mode of these receptors, *i.e.* the binding and release of gaseous SO$_2$ by solid organoplatinum materials, has been studied in more detail and resulted in the development of the first switches that operate in the crystalline state.[3] This implies that adduct formation with SO$_2$ occurs even in densely packed, crystalline material, and that monolayering of the organoplatinum receptors is not required in order to achieve a maximal sensor performance for the heterogeneous detection of atmospheric SO$_2$.

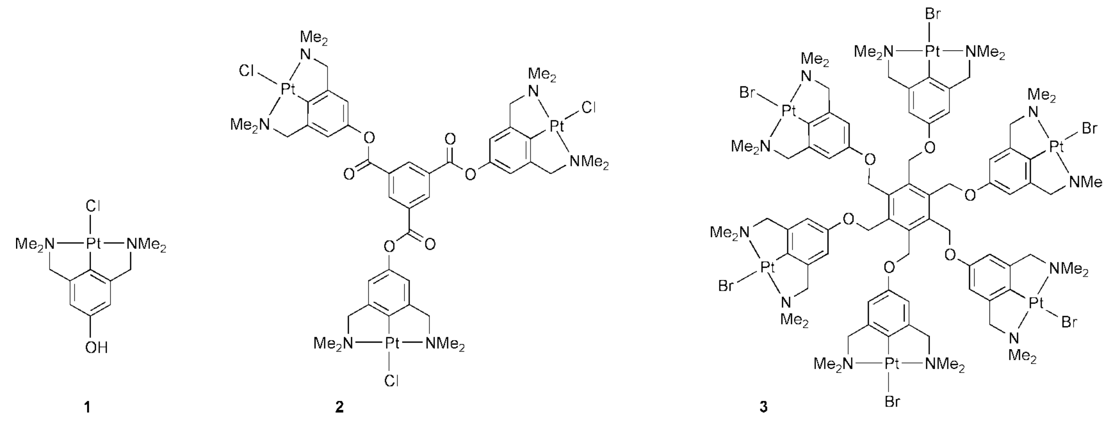
Motivated by these results, a sensor device has been designed which comprises organoplatinum recognition sites and a quartz crystal microbalance (QMB) for signal detection. In such a sensor device, substrate binding is accompanied by a change of the net mass of the surface (host–guest complex *vs.* host only). QMBs are highly sensitive balances which translate small mass changes (typically in the order of nanograms) of the QMB disc into an inverse modification of its resonance frequency, which can readily be recorded.[4]

Attempts to use monometallic organoplatinum complexes similar to **1** (Fig. 1) as receptors failed since these complexes slowly sublime at an operating temperature of 50 °C. These complications were circumvented, however, by using receptor sites that were covalently linked to a macromolecular support. Periphery-functionalised metallodendrimers[5] of low generation are particularly intriguing for these purposes, since they warrant a relatively high amount of functional sites compared to their macromolecular weight. Furthermore, the high regularity and well-defined architecture, both inherent features of dendrimers, allow control of the exact number of metal sites and their reproducible accessibility. These characteristics are essential for quantitative sensor applications and are less pronounced in other macromolecules such as polymers.[6] Therefore, the dendritic macromolecules **2**[7] and **3** were used for QMB coatings.

The synthesis of the metallodendritic macromolecule **3** was accomplished by six-fold etherification of hexa(bromomethyl)benzene[8] with **1**.‡ Notably, platinated phenol **1** has been used rather than the metal-free ligand precursor, thus following a convergent-type synthetic strategy.[9] This ensures the formation of a fully metalated product and avoids the difficulties associated with metal insertion as the last synthetic step, thereby eliminating tedious end-group analysis.[10] Complete etherification of the core molecule is most evidently indicated by the pertinent ^{1}H NMR data of **3**: for example, the benzylic protons of the core molecule shift from δ 4.6 to 5.04 and appear in the expected integral ratio.

The sensor activity of **3** has been unambiguously established. Upon exposure to an environment containing SO$_2$, the initially colourless material immediately turns orange (λ_{max} = 353 nm, ε = 43 100 M^{-1} cm^{-1}; toluene), hence indicating the formation of the corresponding SO$_2$ adduct **4** (Scheme 1). The magnitude of the molecular extinction coefficient suggests that the platinum sites are independent of each other and that inter- or intra-molecular communication between the metal centres is negligible.

Immobilisation of the diagnostic multimetallic species **2** and **3** on QMB discs was accomplished by means of the electrostatic spray method.[4] The discs were coated until a frequency shift of



1 **2** **3**

Fig. 1 Mono- and multi-platinum species used for SO$_2$ detection.

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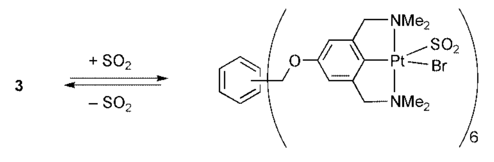
† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b1/b105660n/



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Scheme 1 Mode of action of the hexaplatinated dendritic sensor: reversible η^1-*S*-coordination of SO_2 to the square-planar platinum(II) centre gives a penta-coordinate, intensely orange coloured adduct.

10 kHz was obtained, which corresponds[11] to an average loading of 44 μg cm^{-2} (*i.e.* 29.9 and 14.5 nmol cm^{-2} for trimetallic **2** and hexametallic **3**, respectively, corresponding to 90 and 87 nmol cm^{-2} diagnostic platinum sites, respectively). Upon exposure of such organoplatinum-coated discs to an atmosphere containing SO_2, a decrease of the frequency of the QMBs is observed as a direct response to the change of SO_2 concentration, thus suggesting SO_2 binding to the organoplatinum macromolecules. Control experiments using non-coated QMB discs did not show any frequency modulation and therefore indicate that the disc itself does not interfere with SO_2. A typical plot of the response of these organoplatinum-QMB discs to different SO_2 concentrations is shown in Fig. 2 and demonstrates various characteristics of these sensor devices.

At elevated temperatures (55 °C), quantification of the concentration of SO_2 (generated by mixing N_2 and SO_2) up to 800 ppm is reliable by using **2** (Fig. 2, ESI†). High sensitivity to concentrations as low as 5 ppm is achieved with complex **2** at 35 °C. The lower detection limit for discs coated with **3** is slightly higher (10 ppm at 35 °C), perhaps because of subtle electronic or steric differences in the affinity of the receptor sites to bind SO_2. Clearly, full reversibility of the SO_2 binding is indicated by the straight baseline in experiments performed over a period of several days with either the metallodendritic materials **2** or **3**. This also suggests a high stability of the diagnostic sites. Moreover, the sensor response to changes of SO_2 in the atmospheric constitution is virtually instantaneous, which is in line with previous studies on the reactivity of organoplatinum complexes with SO_2.[3,12] Gas binding on the disc follows saturation kinetics with association constants that are similar to those reported for adduct formation in solution. This indirectly shows that virtually all platinum sites on the disc are sensor-active and that the mode of action in the solid state is the same as in solution.[12]

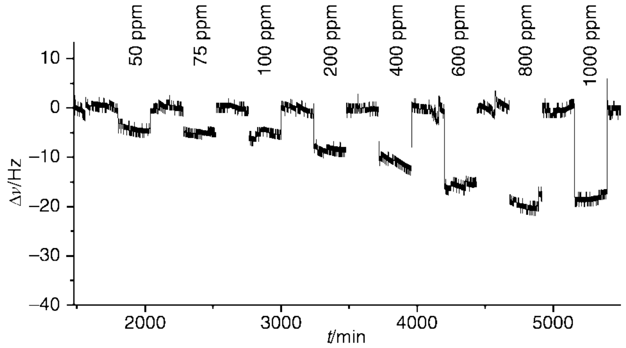

Fig. 2 Frequency change of the QMB disc coated with **2** as a direct response to the change of the SO_2 concentration at 55 °C; between different cycles, the device was purged with nitrogen ($\Delta\nu \approx 0$ Hz).

Another remarkable characteristic of these sensor devices is their direct response to both increasing and decreasing concentrations of SO_2, which eliminates a time-consuming purging of the system to regenerate the receptor sites before each measurement. Notably, regeneration of the sensor-active sites in solution was much slower.[2] Finally, the sensor-active organoplatinum layers are highly selective for SO_2 gas detection. No change of the frequency signal has been observed in cross-experiments with various volatile organic compounds (*e.g.* benzene, toluene, aniline, methanol, nitromethane) or with inorganic gases such as NH_3, CO, CO_2, H_2O as substrates.

In conclusion, efficient sensor devices have been developed which are very selective and robust, and which quantify SO_2 in the ppm concentration range. Notably, the devices presented here are promising archetypes of a new class of sensor materials for a broad range of gases: by using similar mass sensitive techniques paired with different, highly discriminating recognition sites based on transition metals various volatile (in)organic compounds such as CO or NO_x may be selectively detected and quantified even at low concentrations.

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Notes and references

‡ *Synthesis* of **3**: a suspension of **1** (1.31 g, 3 mmol), $C_6(CH_2Br)_6$ (0.32 g, 0.5 mmol), K_2CO_3 (0.83 g, 6 mmol) and 18-crown-6 (80 mg, 0.3 mmol) in acetone (20 mL) was stirred at reflux for 48 h. All volatiles were removed under reduced pressure and the residue was suspended in CH_2Cl_2 (20 mL). After filtration, the filtrate was concentrated to *ca.* 2 mL and treated with Et_2O (20 mL). An off-white precipitate formed, which was collected, washed with Et_2O and dried *in vacuo* to afford 1.18 g (78%) of **3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.40 (s, 12H, C_{aryl}–H), 5.04 (s, 12H, CH_2O), 3.97 (s, 24H, CH_2N), 3.12 (s, 72H, NCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 156.3 (C_{aryl}–O), 144.0 (C_{aryl}–CH_2O), 138.3 (C_{aryl}–Pt), 137.9 (C_{aryl}–CH_2N), 106.4 (C_{aryl}–H), 77.2 (CH_2N), 63.7 (CH_2O), 55.2 (NCH_3); FAB-MS: *m*/*z* 3045.2 $[M+H]^+$ (calc. 3044.8), 2962.8 $[M - Br]^+$ (calc. 2963.9) (Calc. for $C_{84}H_{100}Br_6N_{12}O_6Pt_6 \cdot CH_2Cl_2$: C, 32.63; H, 3.93; N, 5.37. Found: C, 32.48; H, 4.22; N, 5.17%).

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