Research News

Gas Sensor Materials Based on Metallodendrimers**

By Martin Albrecht and Gerard van Koten*

1. Introduction

The design of efficient gas sensor materials, which are characterized by a high selectivity and sensitivity and a good response, is an intriguing challenge in materials science, as no common approach is available that is applicable to the detection of all gases. Nevertheless, particularly medically relevant gases (such as O_2 and CO_2) have attracted considerable attention and can now be detected routinely with commercially available devices.[1] Recent advances have also been achieved in the detection of some volatile organic compounds by means of dendritic or inorganic materials.[2] In contrast to the well-established identification techniques of these substrates, suitable detector materials for SO_2 are barely known.[3] This is surprising as the emission of sulfur-containing compounds, either from natural (phytoplankton, volcanoes) or, increasingly, from anthropogenic (fossil fuel combustion) sources, is a major environmental concern.[4] Sulfur dioxide, a main intermediate in the oxidation cycle of sulfur compounds, is known to have an air pollutant effect and is closely related to smog and acid rain.[5] In the presence of hydrogen peroxide (H_2O_2) it is readily oxidized to SO_3, which spontaneously reacts with humidity from the air (clouds) to form sulfuric acid. From an environmental point of view, fast detection and efficient transport of small amounts of SO_2 that are formed as undesired byproducts during, for example, combustion processes, are beneficial. Hence the development of sensor and carrier materials that detect quickly and bind reversibly even traces of this gas is highly desirable.[6] A potential method for the development of suitable detector materials for the selective recognition of SO_2 gas may be based on a range of transition metal complexes as active units, since SO_2 is known as a versatile ligand in inorganic and organometallic chemistry that can act as either a Lewis base or acid.[7]

It appeared that in particular organoplatinum complexes containing a terdentate coordinating monoanionic "pincer"

ligand $[C_6H_3(CH_2NMe_2)_2-2,6]^-$, abbreviated as NCN, are prime candidates for SO_2 detection as these complexes reversibly bind SO_2 in the solid state and in solution. This occurs via Pt–S η^1 bond formation, and is accompanied by a concomitant color change from colorless to bright orange (Fig. 1).[8] The Pt^{II}–NCN pincer SO_2 adducts are characterized by a pentacoordinate platinum(II) center that displays a formal metal-to-ligand bond. Reversibility of the adduct formation, which is not often observed for transition metal SO_2 complexes, is an inherent prerequisite for the design of carrier and sensor materials. Furthermore, the change of the macroscopic properties, i.e., the observed characteristic color change, upon coordination of SO_2 can serve as a signal transduction device for the molecular recognition of SO_2. These facts suggest these organometallic materials to have potential diagnostic application in SO_2 detection.[9] A characteristic of the organoplatinum complexes that is particularly important for the design of suitable sensor devices is their chemical and physical robustness. The platinum center is kept in a rigid position owing to the terdentate NCN-coordination binding mode of the pincer ligand. This is demonstrated by a strong metal–carbon bond (typical bond length 1.90–1.96 Å). As a result, the Pt–C bond is not affected by air, moisture, or strong acids. Thermal stability has been observed in a temperature range from 150 to 600 K. Increasing the temperature beyond 600 K leads to the formation of decomposition products.

Full recycling of the detection material is a basic issue that must be guaranteed by a suitable sensor device. Recovery without loss of substance or activity may be achieved by anchoring of the active platinum–pincer site on a macromolecular support. This circumvents difficulties associated
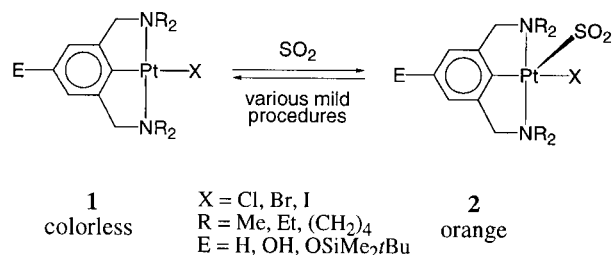

1 colorless	X = Cl, Br, I R = Me, Et, $(CH_2)_4$ E = H, OH, $OSiMe_2tBu$	**2** orange

Fig. 1. Reversible gas adsorption and desorption of Pt^{II} complexes **1** containing the "pincer" ligand via formation of a colored pentacoordinated adduct **2**.

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with selective separation of monomeric platinum complexes from a solution mixture, as the macromolecular sensors are easily recovered by, e.g., filtration or centrifugation techniques.[10] Various frameworks for the attachment of the adsorption active unit may be envisaged, such as immobilization of the monomers on silica (or a similar (heterogeneous) support), monolayering on a surface, connection to a polymer backbone, or suitable functionalization of a dendrimer-type macromolecule. To maintain the advantages of the monometallic complexes (e.g., qualitative and quantitative measurement of the concentration of SO_2), supports with well-defined connectivity patterns are desirable. Hence, functionalized dendrimers are preferred to polymers, where surface congestion and locally reduced accessibility of the diagnostic sites imply inaccuracy.

Dendrimers are tree-like macromolecules that are built up in a highly controlled stepwise manner and therefore have well-defined size, molecular weight, internal connectivity, and a specific number of peripheral end groups.[11] The attachment of the organometallic sensor sites at the periphery of dendrimers can be used as a method of creating metallodendrimers[12] that qualitatively and quantitatively detect SO_2 gas and can be recovered by techniques such as ultrafiltration.

Hence, the realization of metallodendrimer-based sensor materials consists of three parts: i) development of suitable synthetic procedures to prepare metallodendrimers with a well-defined number of peripheral sensor sites; ii) comparison of the sensor activity of the metallodendrimers with respect to monometallic reference materials; iii) verification of the reversibility and recovery properties of the sensor materials and exclusion of reduction of the detector activity (e.g., due to leakage, inactivation) after repeated use.

2. Results

2.1. Synthesis

From preliminary studies on platinum complexes containing the pincer ligand, it is known that the adsorption activity of the metal center and consequently its detection sensitivity for SO_2 is strongly influenced by ligand modifications.[8a] This can be used to vary the electronic and steric properties of the platinum center and thus to optimize the (optical) response of the sensor materials to SO_2. Appropriate substituents R on the nitrogen donors of the pincer ligand (Fig. 1) regulate the accessibility of the metal center for an incoming ligand such as SO_2. Furthermore, only marginal influence on the sensitivity of the metal center has been attributed to *para*-substituents E on the aryl ring of the pincer ligand. Hence, the introduction of appropriate functional groups on this position, e.g., a phenolic hydroxyl group (**1**, E = OH), offers a potential anchoring point for the attachment of the sensor sites to a macromolecular support.

A proper choice of the type of dendrimer used as carrier

framework for the detection-active platinum units unambiguously enhances the performance of the metallodendrimers in filtration applications. For example, a high degree of shape persistence[13] may give satisfactory retention results even for relatively small dendrimers. This reduces the synthetic efforts associated with the preparation of large dendrimers of higher generations. In contrast to the widely studied, flexible carbosilane[14] or alkylamine (poly(aminoamine), PAMAM)[15] backbones, dendrimers containing arylester building blocks[16] show high rigidity. Therefore a dendrimer core has been selected that consists of a benzene center substituted with acid-chloride functionalities as rigid linkage units. Coupling of the modified organoplatinum complexes **1** (E = OH) to the core via esterification reactions thus affords the trimetallic macromolecule **3** with three diagnostic platinum centers at the periphery.[16a] Alternatively, coupling of the monometallic complexes to an appropriate AB_2 branching point containing a (protected) phenol and two acid-chloride groups prior to the attachment to the core unit yields a periphery-functionalized metallodendrimer **4** containing six adsorption-active metal sites (Fig. 2).[9] Molecular modeling suggests for both macromolecules **3** and **4** a disk-like structure with a diameter of 2.4 and 3.4 nm, respectively.

2.2. Activity

Similar to the monomeric platinum complexes, the dendrimers **3** and **4** are very sensitive to SO_2 and indicate its presence instantaneously (within less than 2 ms at 190 K) by a characteristic bright orange color of the corresponding adducts (λ_{max} for the adducts of the metallodendrimers typically around 350 nm ($\varepsilon > 25\,000$ M^{-1} cm^{-1}), shoulder at 410 nm). No protection or pretreatment of the active sites is necessary. This demonstrates a high selectivity of the sensors for SO_2 as neither O_2 nor other gases from the atmosphere (e.g., N_2, CO, CO_2, H_2O) cause a decrease in activity, which may arise due to, for example, competitive adduct formation. Even traces of SO_2 gas are sufficient to induce the typical color change. At a sensor/SO_2 molecular ratio of 1:10 (metallodendrimer **3**), it is possible to detect SO_2 concentrations in solution as low as 100 μM (6 μg SO_2 cm^{-3}) using UV-vis spectroscopy. Nuclear magnetic resonance spectroscopy has proved to be another sophisticated method to monitor and quantify the presence of SO_2, as in solution all platinum centers on the dendrimers are equally active in adsorbing SO_2 (Fig. 3). With solid metallodendrimers, measurement of the artificially increased concentration of atmospheric SO_2 shows similar threshold values. Surface coating with dendritic **3** at a density of 20 nmol mm^{-2} enables the detection of a SO_2 concentration of 8.5 (± 0.5) μg cm^{-3}. Procedures to lower the threshold value to a significant extent and to quantify the concentration of SO_2 more precisely are certainly available, such as using appropriate signal amplification devices and/or more elevated monitoring techniques.
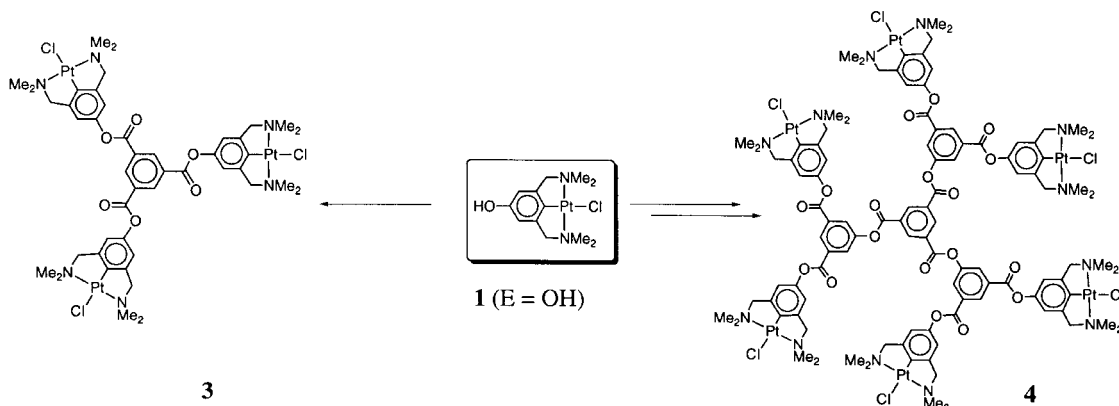
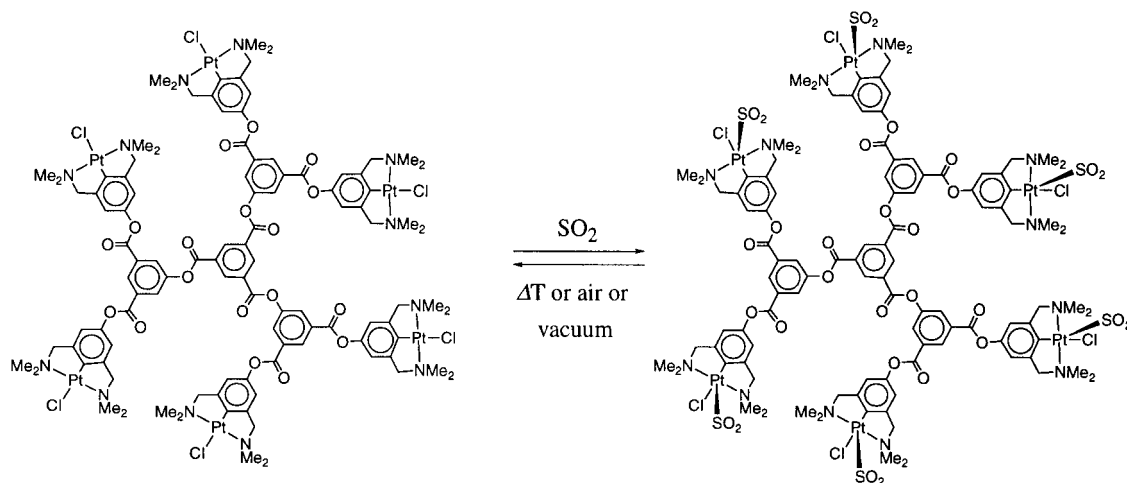Fig. 2. Metallodendrimer-based sensor materials for reversible SO_2 gas detection.

Fig. 3. Sulfur dioxide adsorption activity of the metallodendrimers; all centers are equally active (see [9]).

Sulfur dioxide titration experiments illustrate the versatility of the metallodendrimer sensors (Fig. 4). Whereas monometallic substrates are highly sensitive at a SO_2 concentration up to 0.4 M, a large optical response to small changes in the concentration between 0.6 and 1.6 M is obtained for trimetallic materials. The sigmoidal curve becomes even narrower for the hexametallic detector materials, thus enhancing the resolution in sulfur concentrations between 0.8 and 1.4 M. A combination of core-functionalized monometallic and periphery-functionalized multimetallic dendrimers therefore provides sensor materials that are able to register a broad range of SO_2 concentrations.
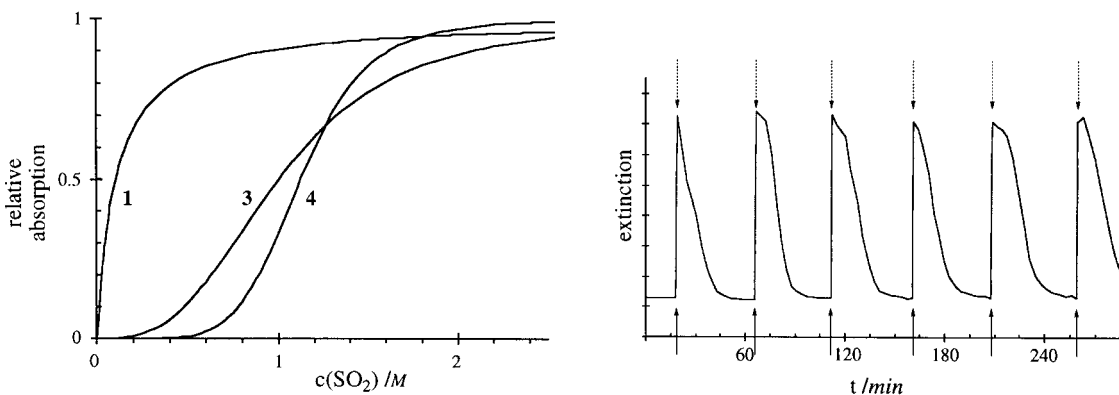

Fig. 4. Left: Idealized absorption curves for SO_2-titration of monometallic (complex **1**, E = H), trimetallic (dendrimer **3**), and hexametallic (dendrimer **4**) sensor materials. Right: Repeated SO_2 adsorption–desorption cycles for dendritic sensor **3** emphasize the stability and the efficiency of the detector material. The arrows mark saturation of the solution with SO_2 (solid) and with air (dashed) (for details, see [8a])

ADVANCED MATERIALS

2.3. Repeated Use

A variety of facile and non-destructive methods are available to recycle the sensor materials. These include chemical (e.g., competitive SO_2 transfer to halide ions or amines[17]) as well as physical (e.g., heating, pressure reduction) removal of SO_2. In addition, saturating the environment with SO_2-poor air for a few minutes regenerates the starting sensor materials quantitatively. This broad selection of procedures makes these platinum-based materials attractive as detectors for repetitive and efficient use.

The full reversibility of the SO_2 adsorption has been verified by repeated adsorption–desorption cycles. The adsorption of a solution containing the sensor materials has been monitored at a fixed wavelength while the solution was saturated alternately with SO_2 and air. The results (Fig. 4) reveal several essential characteristics of a nearly ideal sensor. First, no decrease of the extinction coefficients has been observed even after several cycles, indicating full reversibility. Second, the optical response in the presence of the substrate is fast (instantaneous on laboratory time scale at ambient temperature), and no delay between atmospheric change and signal output is observed. Third, no loss of activity in the recognition of SO_2 is observed, that is to say, the metallodendrimers are chemically persistent under the conditions used in sensor applications.

3. Conclusions and Perspectives

The synthesis of functionalized metallodendrimers offers a general approach to the design of specific and efficient sensor materials for a wide variety of substrates. A proper choice of the (transition) metal center and the corresponding ligand array is crucial since the metal center generally exhibits a high selectivity for particular substances. This enables the preparation of detector materials of a high selectivity. Furthermore, ligand tuning in organometallic complexes can be used as a method to modify and optimize selectivity and sensitivity of the detector units through electronic and steric effects. Ligand fragments that have minor or no influence on the sensor activity may serve as potential anchoring points to immobilize the sensor sites on an appropriate support, e.g., on dendrimers or polymers. In addition, they provide sites for the introduction of signal transduction and amplification devices. Through a suitable fixation of the sensing unit, recovery of the sensors by common separation techniques (e.g., filtration, precipitation, centrifugation) is facilitated.

As a first result, the metallodendrimers **3** and **4** have been prepared as diagnostic materials for SO_2. They are characterized by several properties of an ideal sensor:

- high selectivity towards SO_2
- direct optical response to the presence of SO_2 by a significant color change
- promising resistance against atmospheric impurities (acids, water)
- fast and fully reversible binding of the SO_2 molecule
- high physical persistence over a broad temperature range
- quantitative and diagnostic response
- modification of the detection sensitivity by ligand tuning and by variation of the number of platinum sites on the metallodendrimers (e.g., core or periphery functionalization)

It may be expected that, using the methodology presented here, various other metallodendrimers will be developed that exhibit typical sensor characteristics, such as high sensitivity and excellent selectivity.

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