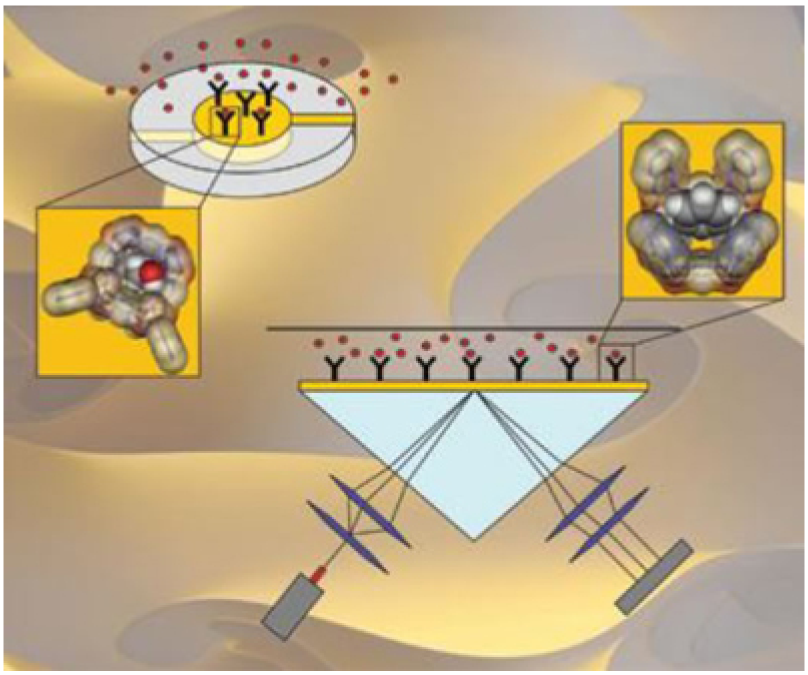
Supramolecular Sensors

Chemical sensors play an increasingly important role in our everyday life: environmental monitoring, industrial process control, quality control of food and beverages, hazardous chemicals, explosives detection and workplace monitoring are just a few examples of their widespread use. In all cases the driving force behind the development of sensor technology is the need for immediate and accurate analyses.

A long-standing problem with chemical sensors is their tendency to give false responses. In sensors that use chemically sensitive coating layers, such false responses are caused by inadequate selectivity towards target molecules. The search for selectivity is therefore one of the key issues in developing new chemical sensors with a significant applicative impact.



"False responses are caused by inadequate selectivity towards target molecules."

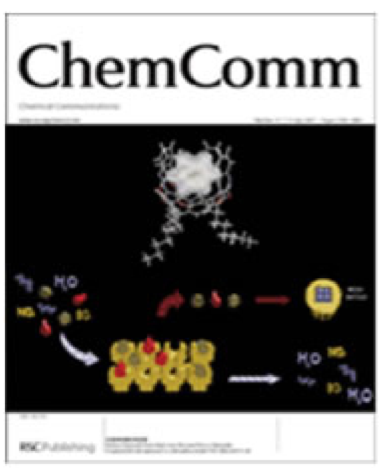
Advances in supramolecular chemistry offer many opportunities to design and prepare molecules endowed with superior molecular recognition properties to be used in chemical sensors. Unfortunately, in most cases the complexation properties of synthetic receptors have been optimized in solution, while their use for gas sensing requires mastering molecular recognition at the gas-solid interface. Molecular recognition in the liquid phase cannot be automatically transferred to vapour and gas sensing, since in moving from the vapour to the condensed phase the analyte experiences a dramatic increase in non-specific dispersion interactions, which are negligible in solution.

Our recent review deals with the design of synthetic molecular receptors capable of recognition at the gas-solid interface, to be used in gas sensors. Cavitands, synthetic organic compounds with enforced cavities of molecular dimensions, have been chosen as a case study to highlight all the necessary steps to prepare an effective supramolecular sensor for organic vapours.

The major obstacle in the development of supramolecular sensors using mass transducers is that both specific binding events that occur within the receptor cavity and non-specific dispersion interactions that occur elsewhere in the layer give rise to responses. The competing presence of non-specific dispersion interactions partially overrides the weak specific ones, threatening sensor selectivity. Another essential feature is the reversibility of the responses, which requires the recourse to weak interactions, since the formation of ionic or covalent bonds would result in an irreversible saturation of the chemical layer. Moreover, the design of the supramolecular receptors for gas and vapour sensing demands the appropriate choice of the weak interactions to be implemented in function to the analytes to be detected.

"Molecular recognition in the liquid phase cannot be automatically transferred to vapour and gas sensing."
For all these reasons a precise receptor design is required, together with a detailed study of the complexation phenomena both in the gas and solid phase. Several steps are needed: first, compelling evidence of analyte complexation within the receptor layer must be obtained via adsorption isotherm measurements. Then, a molecular level understanding of the receptor-analyte interactions has to be acquired. The combined use of mass spectrometry and X-ray crystallography will respectively provide information about the gas phase and solid state interaction modes. If the dominant interactions in the two phases coincide, the knowledge assumes a predictive value for the receptor performances in sensors.
One of the available options to minimize non-specific interactions is the reduction of the receptor layer thickness in connection with an appropriate transducer. Thin layers or, even better, monolayers of molecular receptors have been employed in connection with SPR (surface plasmon resonance) transducers. SPR is an optical phenomenon that provides a safe, remote and non-destructive means of sensing. Thanks to its increased selectivity with respect to the other transduction schemes, SPR can detect vapour interactions with monolayers of molecular receptors. In our review the effectiveness of supramolecular SPR sensing has been shown using cavitands as receptors for volatile aromatic organic vapours. The same approach has been undertaken recently to develop supramolecular SPR sensors to detect a nerve gas simulant with the aim of producing a selective sensor for chemical warfare agents.

Cover gallery:



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