Environmental benzene detection

The fast, widespread and reliable monitoring of carcinogenic compounds at very low concentrations in air constitutes a mandatory goal for environmental and health organizations and a major challenge for the chemical community. Multidisciplinary, innovative solutions are required to overcome the present limits, particularly in benzene detection.

The supramolecular approach to analytical sampling materials can be seen as a noteworthy improvement by imparting selectivity to analytical techniques from one side and by tailoring selectivity of the adsorbed material towards the desired class of analytes from the other side, thus allowing to achieve remarkable analytical results.

Molecular recognition is a recurrent theme in chemical sensing because of the importance of selectivity for sensor performances. The popularity of molecular recognition in chemical sensing has resulted from the progress made in mastering weak interactions, which has enabled the design of synthetic receptors according to the analyte to be detected. However, the availability of a large pool of modular synthetic receptors so far has not had a significant impact on sensors used in the real world. This technological gap has emerged because of the difficulties in transferring the intrinsic molecular recognition properties of a given receptor from solution to interfaces and in finding high fidelity transduction modes for the recognition event. The work proposed for the Award fills this gap in the case of environmental monitoring of toxic aromatic VOC.

Selective monitoring of airborne aromatic volatile organic compounds (VOC) in air, namely BTEX (benzene, toluene, ethyl benzene and xylenes), is both socially relevant and technologically challenging, since high-precision measurement at trace concentrations of these nonpolar molecules is generally interfered with by overwhelming amounts of aliphatic hydrocarbons. Presently, real-time air monitoring is performed by bulky conventional laboratory equipment that incurs high operating costs and requires trained users. Simple low-cost systems based on solid state gas sensors were recently proposed, the most important being Metal OXide sensors (MOX), Quartz MicroBalances (QMB), Surface Acoustic Waveguides (SAW), and polymeric sensors. These technologies have often reached sufficient sensitivity for the detection of the target gas species, but generally their selectivity is limited and not sufficient for reliable quantification or early-warning systems. However, these are not viable solutions for stand-alone sensors for urban monitoring. Multisite urban monitoring of benzene needs simple yet selective systems to be embedded in traffic lights or lampposts, without maintenance service. The exploitation of molecular receptors as sensing materials is particularly attractive to address the selectivity issue. The progress made in designing synthetic receptors enables the modulation of the sensor selectivity towards different classes of compounds by mastering the weak interactions occurring between the sensing material and the analytes. The selective aromatic hydrocarbon complexation properties of tetraquinoxaline cavitands (QxCav) have been exploited in our group to fabricate low-cost systems with sub-ppb_v detection limits of toxic volatile organic compounds (VOCs) in the presence of other airborne pollutants (see Dalcanale et al. *Chem. Commun.* **2007**, 2790-2792, highlighted with Inside cover and Chemical Technology Highlight; *Chem. Commun.* **2010**, *46*, 288-290). The performance of this prototype is enabled by a pre-concentrator unit filled with Quinoxaline Cavitand (QxCav) molecules capable of selectively trapping aromatic vapors at the gas-solid interface. The receptor cavity is able to discriminate aromatic from aliphatic hydrocarbons due to the formation of specific interactions like CH-π and π-π interactions. The selective hosting properties of tetraquinoxaline cavitands (QxCav) towards aromatic hydrocarbons have been proven in gas phase as well as in the solid state. Rational design of QxCav molecular structures offers the possibility to further improve both the sensitivity and the selectivity of the preconcentrator (see Dalcanale et al. *CEJ* **2018**, *24*, 1010-1019).