



# Cavity-containing rhenium metallacycle treated evanescent wave infrared chemical sensors for the selective determination of odorous amines in the atmosphere



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## ABSTRACT

An evanescent wave infrared chemical sensor was developed for the selective detection of odorous amino compounds in the atmosphere. To achieve this goal, cavity-containing rhenium metallacycles with multi-recognition sites were prepared and used as host molecules to modify the surface of an evanescent wave infrared (EWIR) sensing element. The unique cavity structure with hydrophobic properties of the Re metallacycle permits the selective trapping of suitably sized compounds with proper functionalities. To explore the scope of the process, two different Re metallacycles were synthesized and used to trap a series of volatile organic compounds (VOCs) with different functionalities. Based on the results, Re metallacycles are selective to detect amino compounds as evidenced by the peak shifts for C=O absorption after the amino compounds had been adsorbed. The hydrophobic pocket and hydroxyl groups in the Re metallacycles were also verified to provide extra forces to stabilize the attraction of amino compounds. The efficiency of the Re metallacycles in detecting amino compounds follows the order of amine with phenyl ring > aliphatic primary amine ~ cyclo-amine > aliphatic secondary amine > aliphatic tertiary amine. This sensor was applied to detect benzyl amine and a linear range up to 1 mg/L could be obtained with a detection limit close to 4 μg/L.

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## 1. Introduction

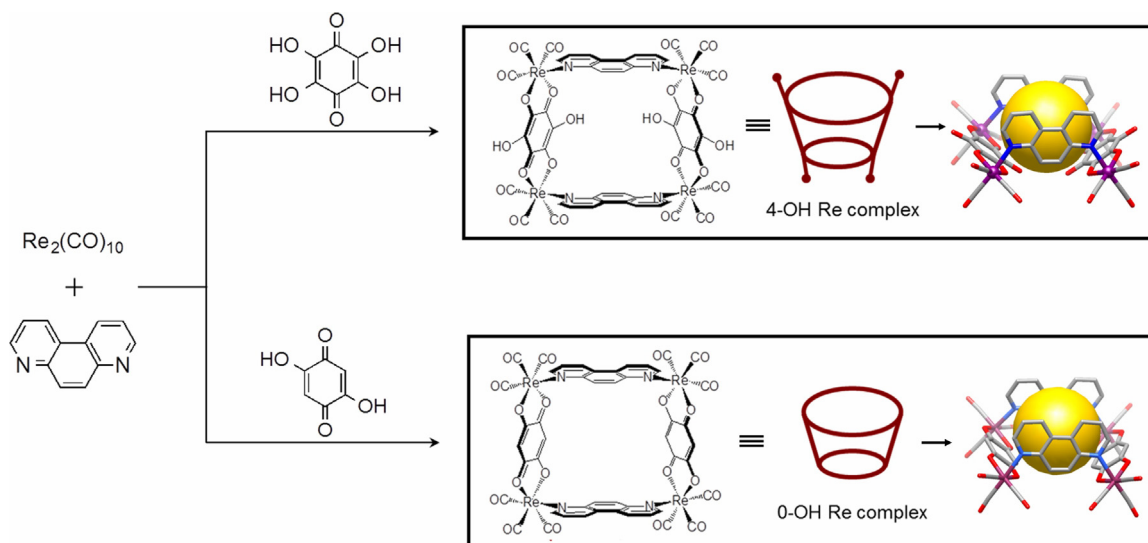
The determination of odorous amino compounds in the atmosphere is an important task because it is crucial for preventing possible diseases and to rectify the unpleasant environment caused by the presence of amines [1,2]. A large number of analytical methods have been developed to determine the concentration of amines in different matrices. Assays based on a quartz crystal microbalance have been widely applied [3,4]. Optical systems such as colorimetric [5,6], near infrared (NIR) [7], UV/Vis absorption [8,9], and fluorescence spectroscopy [10,11], have also been used for the determination of amino compounds. Alternatively, separation [12–15] and electrochemical methods [16,17] have also been

reported for this purpose. However, the tedious procedures related to detection and the low selectivity in the detection of amino compounds limit the applications of these methods to air samples. To address, we developed a selective and sensitive infrared sensing method based on evanescent wave IR (EWIR) spectroscopy [18]. In this method, a Re metallacycle is synthesized and integrated with EWIR as a selective phase to concentrate odorous amino compounds in the atmosphere for detection.

In the past few decades, considerable interest has developed in the assembly and self-assembly of supramolecules, including transition-metal-based “molecular squares” [19–22], calix[n]arene [23–26], porphyrins [27–30], and crown ethers [31–33]. Due to the multiple characteristics of supramolecules, such supramolecules are widely utilized in the fields of sensors [34,35], probes [36], molecular recognitions [37,38], photonic devices [39], catalysts [40,41] and host-guest chemistry [42,43]. Although it has been proposed that such materials should have widespread applications,

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**Fig. 1.** Scheme showing the self-assembly of the 4-OH Re and 0-OH Re metallacycles.

the actual utilization of such unique materials in combination with infrared spectroscopy are rarely reported. To integrate the unique properties of supramolecules into IR sensing technology, cavity-containing tetrarhenium metallacycles with multiple recognition sites were designed, synthesized, and used as host molecules to selectively attract amino compounds in the atmosphere. The modification of this type of compounds on the IR sensing elements can significantly improve the sensitivity and selectivity in the detection of amino compounds. Fig. 1 shows the schematic diagram for the synthesis of the designed rhenium complexes used in this work. Dirhenium decacarbonyl, dhbq and 4,7-phen are assembled to form a tetrarhenium complex (0-OH Re metallacycle). This complex contains a cavity that is designed for recognizing a suitably sized molecule. If the dhbq is changed to thq, the rhenium complexes (4-OH Re metallacycle) with 4 hydroxyl groups were formed.

## 2. Experimental section

### 2.1. Chemicals

Dirhenium decacarbonyl ( $\text{Re}_2(\text{CO})_{10}$ ), 4,7-phenanthroline, 2,3,5,6-tetrahydroxy-1,4-benzoquinone (thq), and 2,5-dihydroxy-1,4-benzoquinone (dhbq) are purchased from Acros Organics (Phillipsburg, NJ) and are used in the synthesis of tetrarhenium metallacycles. Various volatile organic compounds (VOCs) with different characteristics are used in examining the guest discriminability of the tetrarhenium metallacycles, including butylamine, butanethiol, bromobutane, butanol, toluene, benzaldehyde, chlorobenzene, nitrobenzene, benzylamine, aniline, acetophenone, ethylamine, amylamine, hexylamine, cyclohexylamine, dipropylamine, triethylamine, pyridine, and phenethylamine were purchased from TEDIA (Fairfield, OH). All chemicals were used as received without further purification. A  $45^\circ$  trapezoidal (55 mm  $\times$  5 mm  $\times$  2 mm) zinc selenide internal reflection element obtained from international crystal laboratory (Garfield, NJ) was used.

### 2.2. Apparatus

The sample cell is made by stainless steel with a dimension of 30 mm  $\times$  30 mm  $\times$  100 mm, which has a cell volume of 90 cm<sup>3</sup>. Detail of this sample cell has been described in our previous study [44]. A thick Teflon film was used to seal the sample cell and can be

tightened to the cell body by screws. The formed sampling setup is placed into the sample compartment of an Avatar 370 FT-IR spectrometer (Thermal Nicolet Co., Madison, WI) equipped with a medium-range mercury-cadmium-telluride (MCT) detector. All of the spectra were detected by co-adding 100 scans with 4 cm<sup>-1</sup> resolution.

### 2.3. Preparation of tetrarhenium metallacycles

A mixture  $\text{Re}_2(\text{CO})_{10}$  (65.2 mg, 0.1 mmol), 4,7-phenanthroline (4,7-phen, 18.1 mg, 0.1 mmol), and 2,5-dihydroxy-1,4-benzoquinone (dhbq, 15.5 mg, 0.11 mmol) in *p*-xylene (16 mL) was sealed in a Teflon-lined stainless-steel Parr acid digestion bomb and heated to 180 °C for 72 h, and then allowed to slowly cool to room temperature. The resulting dark-green crystals were separated by filtration, washed with *p*-xylene, and then dried in air. The 0-OH Re metallacycle,  $[\{(\text{CO})_3\text{Re}\}_4(\text{dhbq})_2(4,7\text{-phen})_2] \cdot 1.5\text{C}_8\text{H}_{10}$ , was obtained in 60.6% yield (104.2 mg, based on  $\text{Re}_2(\text{CO})_{10}$ ). IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}} = 2024, 1910, 1898$ ;  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 9.31$  (dd,  $J_{\text{H}^3\text{H}^2} = 8.5$  Hz,  $J_{\text{H}^3\text{H}^1} = 1.2$  Hz, 2H, H<sup>3,8</sup>), 9.03 (dd,  $J_{\text{H}^1\text{H}^2} = 4.4$  Hz,  $J_{\text{H}^1\text{H}^3} = 1.2$  Hz, 2H, H<sup>1,10</sup>), 8.19 (s, H<sup>5,6</sup>), 7.78 (q,  $J_{\text{H}^2\text{H}^1} = 4.4$  Hz,  $J_{\text{H}^2\text{H}^3} = 8.5$  Hz, 2H, H<sup>2,9</sup>), 5.78 (s, H<sup>a</sup>). Anal. Calc for  $(\text{Re}_4\text{C}_{48}\text{H}_{20}\text{N}_4\text{O}_{20}) \cdot 1.5\text{C}_8\text{H}_{10}$ : C 38.40, H 1.88, N 2.99. Found: C 37.98, H 1.84, N 3.02. For the 4-OH rhenium metallacycle,  $[\{(\text{CO})_3\text{Re}\}_4(\text{thq})_2(4,7\text{-phen})_2] \cdot 2\text{C}_7\text{H}_8$ , the dhbq was replaced by tetrahydroxy-1,4-quinone (thq). The preparation of this complex has been described in detail in our previous publication [45].

The 0-OH Re metallacycle crystallized in the triclinic space group *P*, the asymmetric unit consisted of two fac- $\text{Re}(\text{CO})_3$  corners, one dhbq ligand, one 4,7-phen ligand and one *p*-xylene molecule trapped within the cavity. Each rhenium atom is bound to three carbonyl carbon atoms, two oxygen atoms of the dhbq ligand, and one pyridyl nitrogen atom of the 4,7-phen ligand in a distorted octahedral orientation. Two 4,7-phen and two dhbq moieties alternately bridge four fac- $\text{Re}(\text{CO})_3$  modules to form a metallacycle molecule. 0-OH and 4-OH are cyclic tetrarhenium(II)-based molecules with rigid calixlike structures. The formed cavity size was calculated using Diamond software [46]. In 0-OH Re complex, the distance between the upper rims of two 2,5-dihydroxy-1,4-benzoquinone ligands is 10.22 Å and between the lower rims of the same ligands is 5.60 Å. The dimensions of the upper rim is 6.85 Å  $\times$  10.22 Å and the lower rim is 7.66 Å  $\times$  5.60 Å. In 4-OH Re metallacycles, the carbon atoms in the upper rims of two opposite 2,3,5,6-tetrahydroxy-1,4-

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