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Gondola-shaped tetra-rhenium metallacycles modified evanescent wave infrared chemical sensors for selective determination of volatile organic compounds

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ABSTRACT

Water-stable and cavity-contained rhenium metallacycles were synthesized, and their ability to selectively interact with volatile organic compounds (VOCs) systematically studied using attenuated total reflection infrared (ATR-IR) spectroscopy. Integrating the unique properties of rhenium metallacycles into optical sensing technologies significantly improves selectivity in detecting aromatic compounds. To explore the interaction of rhenium metallacycles with VOCs, the surface of ATR sensing elements was modified with the synthesized rhenium metallacycles and used to detect VOCs. The results indicate that rhenium metallacycles have crown ether-like recognition sites, which can selectively interact with aromatic compounds, especially those bearing polar functional groups. The IR absorption bands of rhenium metallacycles shift significantly upon adsorption of aromatic VOCs, revealing a strong interaction between the tetra-rhenium metallacycles and guest aromatic compounds. Optimizing the thickness of the metallacycles coated on the surface of the sensing element led to rapid response in detection. The dynamic range of response was generally up to 30 mg/L with detection limits *ca.* 30 μg/L. Further studies of the effect of interferences indicate that recovery can be higher than 95% for most of the compounds tested. The results on the flow-cell device indicated that the performances were similar to a static detection system but the detection of VOCs can be largely simplified.

1. Introduction

Analysis of volatile organic compounds (VOCs) in gas phase samples is important for environmental monitoring in a variety of situations. VOCs such as benzene, xylene, and toluene are known or suspected to cause chronic adverse health effects including asthma, allergies, and cancer [1,2]. Due to the importance of concentration monitoring of VOCs in the atmosphere, a number of analytical methods have been developed for this purpose. For instance, gas chromatography with mass spectrometry detection (GC–MSD) is frequently used for determination of VOCs in air. Through various techniques of pre-concentration, such as the membrane-introduced method [3,4], solid-phase microextraction [5,6], adsorbents [7,8] and others [9,10], GC–MSD methods provide high sensitivities. However, analysis time is restricted by the nature of separation. Also, the high maintenance and instrumentation costs limit the widespread application of this approach for real-time monitoring. Alternatively, infrared spectroscopic methods also have been developed to detect sub-ppmv levels of VOCs in the atmosphere due to their simplicity and speed of detection. To detect and quantify low concentrations of VOCs in air, gas cells having long path lengths are typically used to improve detection limits. For example, a gas cell having a path length longer than 1 km has been proposed for IR absorption measurements [11]. With proper mathematical treatment of strongly interfered IR spectra, an open-path IR system also can be suitable for on-site VOC monitoring [12]. Similarly, an IR hollow waveguide has been developed to detect low levels of organic species in atmospheric samples [13,14]. The use of attenuated total reflection (ATR) mode is another approach to detect low levels of species of interest in gas phase samples. Because of the short interaction length of an evanescent field with gas on the surface of internal reflection elements (IREs), the number of reflections becomes critical to having a useful optical path length. A long, small-diameter IR optical fiber can be used as an ATR element to enhance the sensitivity of this type of detection. For example, a silver halide optical fiber equipped with a lead-salt-tunable infrared laser has been used to detect SF_6 [15]. Sieber and Muller demonstrated that an evanescent field waveguide also can be fabricated in the form of a chip and used to detect air pollutants [16,17]. This type of chip contains a 1 m long waveguide within a 1 cm^2 area, which is fabricated on single-crystal silicon. Pre-concentration techniques

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are also applied to IR sensing technologies. For example, after coating the IREs with a hydrophobic thin film, organic species can be attracted and concentrated close to the IREs to effect IR detection [18–24]. Because of the hydrophobic nature of the thin film coating on the surface of the sensing element, detecting compounds with polar functional groups is difficult. In addition, the selectivity is also limited in this type of detection as it depends mainly upon the specific IR absorption bands of the sample molecules. To overcome these weaknesses while retaining the ease of signal enrichment of internal reflection methods, we propose the use of cavity-contained recognition host sites as a sensing material to increase selectivity in detecting targeted VOCs.

Self-assembled transition-metal-based "molecular squares" have gained significant attention [25–29] because of their potential in numerous applications, including use as sensors [30,31], probes [32], photonic devices [33], catalysts [34–36] and in host–guest chemistry [37–39]. In this study, cavity-contained tetra-rhenium metallacycles were designed, synthesized, and used as host molecules to increase sensitivity and selectivity for detection of VOCs. The tetra-rhenium metallacycle exhibits a unique cavity to trap molecules within a certain size range and can therefore increase selectivity. Because infrared spectroscopy provides chemical information about the host–guest interaction, a clearer understanding of the recognition mechanism in host–guest chemistry is expected.

2. Experimental

2.1. Chemicals

$Re_2(CO)_{10}$ (di-rhenium deca-carbonyl), 2,5-bis(tert-butyl-2-benzoxazolyl)-thiophene (tpbb), 1,2,4-trihydroxyl-9,10-anthraquinone (H_2-thaq), and diethyl benzene were purchased from Acros Organics (Phillipsburg, NJ) and used in the synthesis of tetra-rhenium metallacycles. Fourteen volatile organic compounds with varying characteristics were selected to examine the specific interactions with tetra-rhenium metallacycles. These compounds included toluene, 1,2,4-trichlorobenzene, chloroform, carbon tetrachloride, trichloroethylene, chlorobenzene, methanol, ethanol, acetone, ethyl acetate, nitrobenzene, acetophenone, benzene, and benzaldehyde, which were all purchased from TEDIA (Fairfield, OH). All chemicals were used as received. A 45° trapezoidal (55 mm × 5 mm × 2 mm) zinc selenide (ZnSe) crystal obtained from International Crystal Laboratory (Garfield, NJ) was used as the internal reflection element for coating with the tetra-rhenium metallacycle.

2.2. Apparatus

A 45° trapezoidal (55 mm × 5 mm × 2 mm) zinc selenide was used as the internal reflection element. Compared the signals from transmission measurement, the number of internal reflection for this internal element is around 12. A static detection system and a flow-cell design were used in this work as shown in Fig. 1A and B, respectively. These devices were placed in the sample compartment of FT-IR spectrometer (Vector 22, Bruker Optics, Ettlingen, Germany) equipped with a mercury–cadmium–telluride (MCT) detector. For static detection system, the sample cell was constructed from stainless steel and had a sample volume of 100 mL. The IRE was placed in the center of the cell as indicated in Fig. 1A. The spectra for this device were detected from 64 scans at a resolution of $4\,cm^{-1}$. For flow cell device, the ZnSe crystal was sandwiched in two aluminum plates as shown in Fig. 1B. A spacer of poly(tetrafluoroethylene) in thickness of 1.5 mm was placed on the top of the ZnSe crystal to form a flow channel. A flow selection switch was used to deliver VOCs and purge nitrogen gas. Spectra were detected from 8 scans at a resolution of $4\,cm^{-1}$.

2.3. Preparation of tetra-rhenium metallacycle

The details of tetra-rhenium metallacycle preparation were described previously [40]. Briefly, after refluxing a mixture of $Re_2(CO)_{10}$, 2,5-bis(5-ter-butyl-2-benzoxazolyl)thiophene and 1,2,4-tri-hydroxyl-9,10-anthraquinone (in a 1:1:1 molar ratio) in diethyl benzene for 2 h, green tetra-rhenium metallacycle precipitates were obtained, separated by filtration, and washed with hexane. The purified tetra-rhenium metallacycle was dissolved in benzene to prepare coating solutions with different concentrations of tetra-rhenium metallacycle. Fig. 2 shows the self-assembly scheme of rhenium-based metallacycle used in this study. The structure of the synthesized rhenium-based metallacycle is also shown in Fig. 2 by space-filling and ball-and-stick representations. According to the previous study [40], the size of the hydrophobic cavity was 5.6 Å × 7.0 Å × 17.8 Å. Different concentrations of tetra-rhenium metallacycle solution in a volume of 60 μL were coated on both sides of the IREs using a micro pipet. The treated IREs were air-dried in the fume hood for at least 20 min before sealed into the sampling cell. After detections, the IREs were regenerated by leaving the sample cell uncapped for a specified period of time with a 60 °C air flow. The IR signals of the residual adsorbed molecules disappeared completely within a 10 min regeneration time for all the VOCs tested by static detection system.

3. Result and discussion

3.1. Basic sensing properties of tetra-rhenium metallacycle modified IREs in the detection of VOCs.

To explore the capabilities of tetra-rhenium metallacycle modified IREs for detection of VOCs, the IR spectra of synthesized tetra-rhenium metallacycle and the raw materials for self-assembling – including di-rhenium deca-carbonyl, 2,5-bis(tert-butyl-2-benzoxazolyl)-thiophene, and 1,2,4-tri-hydroxyl-9,10-anthraquinone – were first examined by coating 60 μL of each of the compounds (0.5%, w/v) onto the IREs. After the solvent evaporated, IR spectra were acquired and plotted in Fig. 3A. To explore the sensing properties of the tetra-rhenium metallacycle, a series of VOCs with varying characteristics were tested. The VOCs tested included ethanol (high polarity), chloroform (low polarity), and chlorobenzene (aromatic). For comparison, the spectra of these compounds were also acquired using a conventional ATR method. The resulting spectra are plotted in Fig. 3B.

Comparing the spectra of the compounds tested, the CO stretching vibrations of tetra-rhenium metallacycle [41–43], originally located at $2025\,cm^{-1}$ and $1930\,cm^{-1}$, were shifted to $2014\,cm^{-1}$ and $1909\,cm^{-1}$ after adsorbing chlorobenzene and ethanol, respectively. The peak shifts of structure-sensitive CO stretching modes, caused by increased π-back-bonding from the Re to CO molecule, provide additional evidence of the interactions between the analyte molecules and tetra-rhenium metallacycle [44–47].

To test for selectivity in detection of VOCs, the band intensities were extracted from the spectra and plotted against the time as shown in Fig. 4A. Generally, more than 20 min was needed for chlorobenzene to reach a constant signal, but only 10 min was required for ethanol to reach the maximum signal intensity. In terms of detected signals, chlorobenzene showed the most intense signal among the test compounds. As observed from the detected spectra, both chlorobenzene and ethanol can cause the shifts of absorption bands of tetra-rhenium metallacycle in the region around $2000\,cm^{-1}$. This indicates that both compounds can

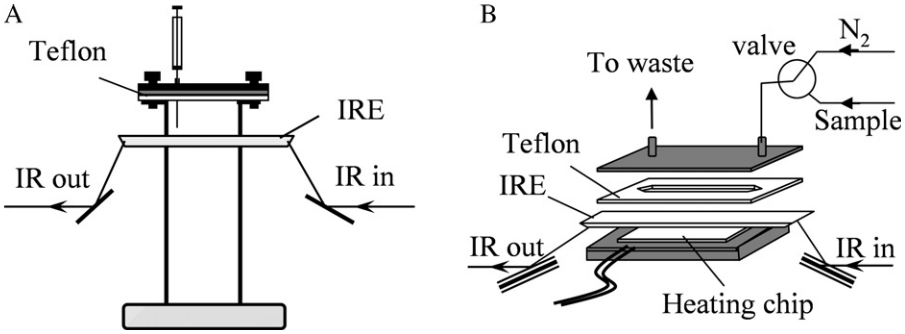

Fig. 1. Schematic representation of the static sensing system (A) and the flow cell device for dynamic detections (B).

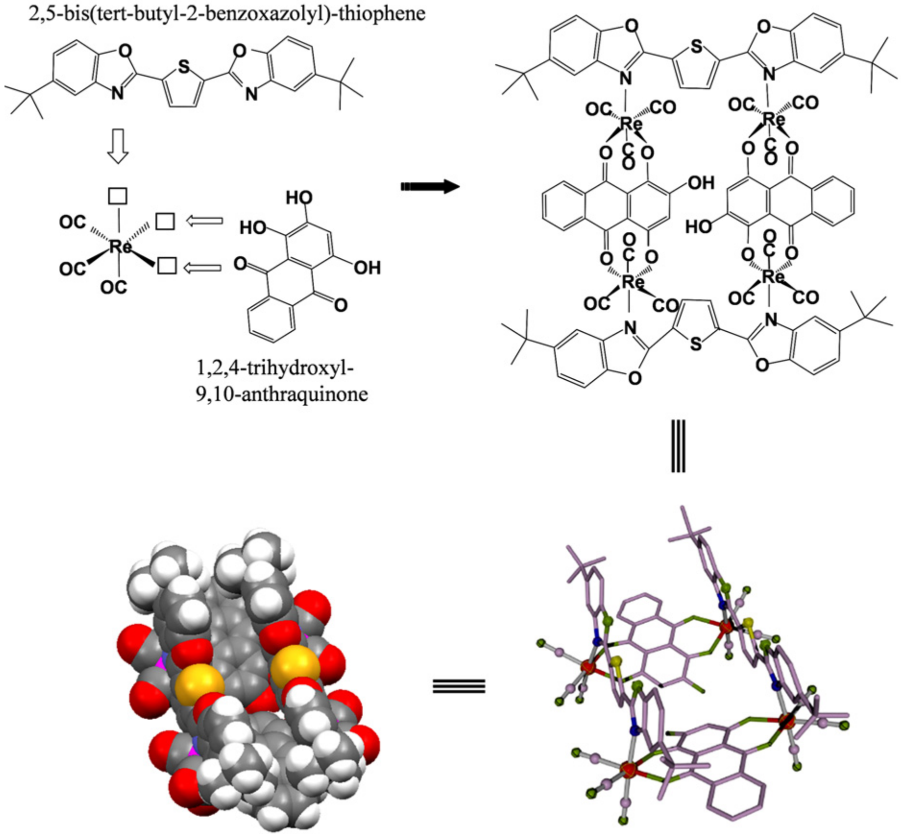

Fig. 2. Self-assembly scheme of rhenium-based metallacycle and the space-filling and ball and stick representations for the synthesized metallacycle.

interact with tetra-rhenium metallacycle. However, because of the small size, ethanol does not fit well within the cavity formed in the tetra-rhenium metallacycle. This may be the reason that much lower intensity was observed in the detection of ethanol compared to chlorobenzene.

3.2. Contribution of the cavity in the tetra-rhenium metallacycle in the detection of VOCs

As described in the previous section, an intense analytical signal was observed in the detection of chlorobenzene using the tetra-rhenium metallacycle sensor. The strong signals might be caused by a simple π–π interaction between phenyl groups in the metallacycle and the test molecules, or an interaction between the functional groups of the metallacycle and the test molecules. To evaluate the contribution of the crown ether-like recognition site formed in the tetra-rhenium metallacycle in attracting VOCs, the bridged ligands used to synthesize the tetra-rhenium metallacycle – including di-rhenium deca-carbonyl, 2,5-bis(tert-butyl-2-benzoxazolyl)-thiophene and 1,2,4-trihydroxyl-9,10-anthraquinone – were each coated separately on the surface of the ATR element, then exposed to chlorobenzene. The time profiles of IR absorption by chlorobenzene using the tetra-rhenium metallacycle and its bridge ligands are plotted in Fig. 4B. The ability of each bridged ligand to detect chlorobenzene is much more limited than that of the assembled metallacycle. These results indicate that the crown ether-like recognition site formed by the tetra-rhenium metallacycle plays the most important role in the adsorption of VOCs. The results also reveal that the tetra-rhenium metallacycle favors interactions with molecules of a size that is compatible with the size of the cavity.

3.3. Selectivity in the detection of VOCs

To further examine the selectivity of the tetra-rhenium metallacycle in detecting VOCs, a series of VOCs bearing different functional

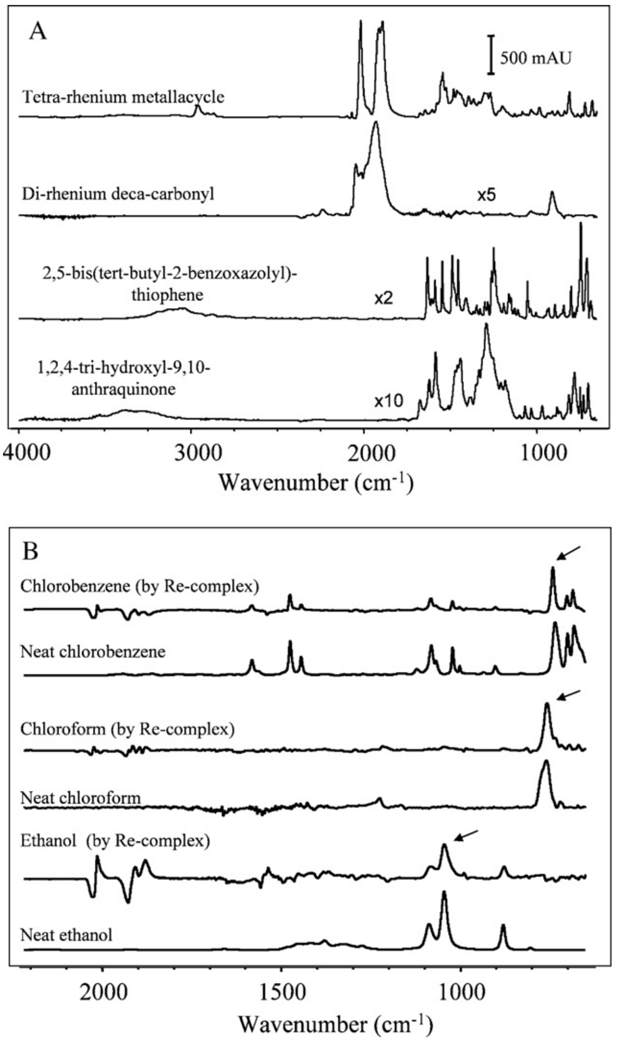

Fig. 3. (A) Infrared spectra of the rhenium-based metallacycle and its bridging ligands. Top to bottom: tetra-rhenium metallacycle, di-rhenium deca-carbonyl, 2,5-bis(tert-butyl-2-benzoxazolyl)-thiophene, and 1,2,4-tri-hydroxyl-9,10-anthraquinone. (B) Typical spectra of chlorobenzene, chloroform, and ethanol detected by IRE coated with tetra-rhenium metallacycle. The neat spectra of each compound were measured with an uncoated IRE.

groups was examined using the assembled metallacycle film on an ATR element. As noted previously, these VOCs included both non-aromatic and aromatic compounds. Non-aromatic compounds included chloroform, carbon tetrachloride, trichloroethylene, acetone, ethyl acetate, methanol, and ethanol. Aromatic compounds included benzene, toluene, chlorobenzene, and trichlorobenzene. After injection of each of the compound to form a concentration of 50 mg/L, spectra were acquired. Typical spectra of the examined VOCs are shown in Fig. 5. According to the peak height of the most intense vibrational mode of each compound, the signal intensities of the examined compounds were tabulated as Table 1. The results show that the signals of aromatic compounds were generally more intense than those of non-aromatic compounds, indicating that the cavity in the tetra-rhenium metallacycle used in this study is selective for aromatic compounds.

3.4. *Optimization of thickness of tetra-rhenium metallacycle in detection of VOCs*

With regard to the detection of organic volatile compounds, the sensitivity and the time required to reach maximum signals is expected to be related to the thickness of the tetra-rhenium metallacycle layer. To determine the optimal thickness of the tetra-rhenium metallacycle, 60 μL of different concentrations of tetra-rhenium metallacycle solutions were prepared and used to coat both sides of the IREs. The resulting sensors were then used to detect 10 mg/L of chlorobenzene. The highest concentration of metallacycle tested was limited to 2% (w/v) because of the solubility of the metallacycle. Fig. 6A shows the absorption time profiles for chlorobenzene adsorbed by different concentrations of tetra-rhenium metallacycle. Fig. 6A shows that more intense analytical signals were obtained as the amount of coated tetra-rhenium metallacycle was increased. Also, the time required to achieve the

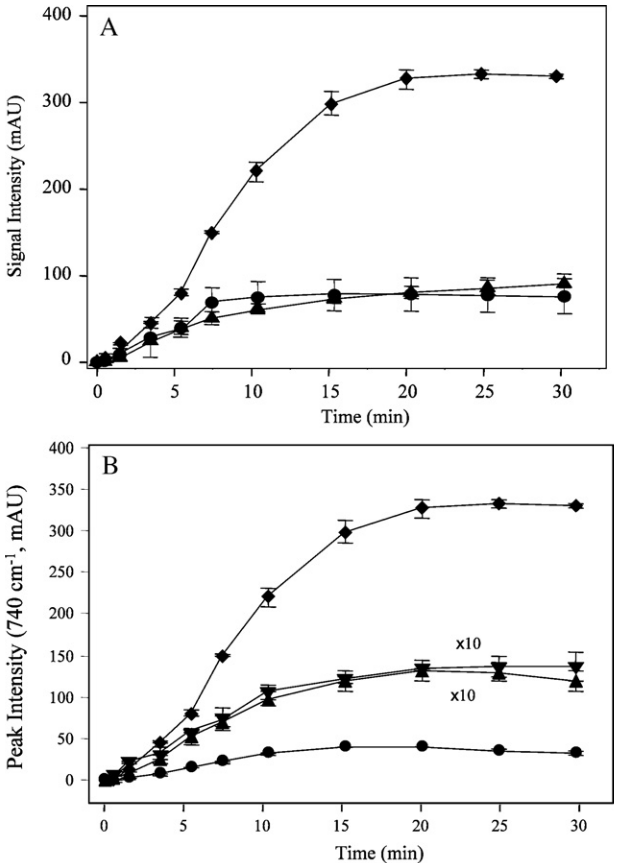

Fig. 4. (A) Time profiles for absorption of chlorobenzene (◆), chloroform (●), and ethanol (▲) in concentration of 0.50 mg/L; the 0.5% (w/v) metallacycle solution was used to modify the surface of IRE. The intensities of the bands labeled with an arrow in Fig. 3B were calculated and used as signal intensity. (B) Detection time profiles for chlorobenzene (50 mg/L) detected by assembled tetra-rhenium metallacycle (◆), di-rhenium deca-carbonyl (●), 2,5-bis-(tert-butyl-2-benzoxazolyl)-thiophene (▲), and 1,2,4-trihydroxyl-9,10-anthraquinone (▼). Signals obtained by 2,5-bis-(tert-butyl-2-benzoxazolyl)-thiophene and 1,2,4-trihydroxyl-9,10-anthraquinone were enlarged 10 times for clarity.

Table 1

Detected signals of examined VOCs. Sensing element is prepared by coating of 60 μL 0.5% (w/v) tetra-rhenium metallacycles on the dual sides of the sensing element. The concentrations of the examined compound are kept 50 mg/L and the signals are taken at 20 min after injection of compounds.

Non-aromatic compound	Signal (mAU)	Aromatic compound	Signal (mAU)
Chloroform	86.3 ± 1.3	Benzene	88.5 ± 2.6
Carbon tetrachloride	27.1 ± 0.6	Toluene	50.2 ± 1.9
Trichloroethylene	78.4 ± 2.5	Chlorobenzene	331.7 ± 5.0
Methanol	48.2 ± 0.1	Trichlorobenzene	268.5 ± 1.3
Ethanol	74.6 ± 2.0	Nitrobenzene	903.1 ± 4.1
Acetone	55.6 ± 4.5	Acetophenone	758.1 ± 12.7
Ethyl acetate	63.1 ± 2.0	Benzaldehyde	560.7 ± 3.6

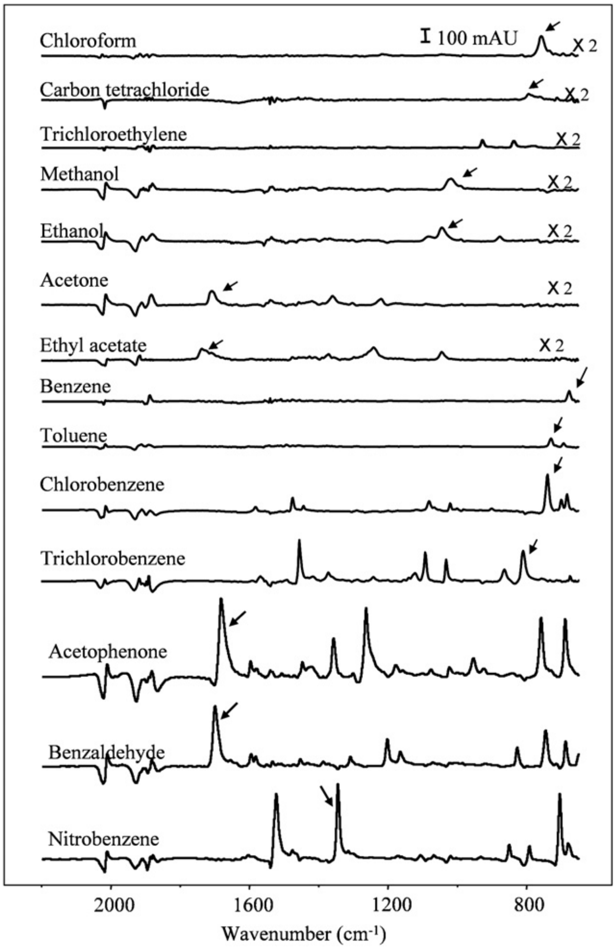

Fig. 5. IR spectra of VOC detected. The concentration of each VOCs was 50 mg/L; IREs were coated with 0.5% (w/v) metallacycle solution. Bands labeled with an arrow were used for quantitative purpose.

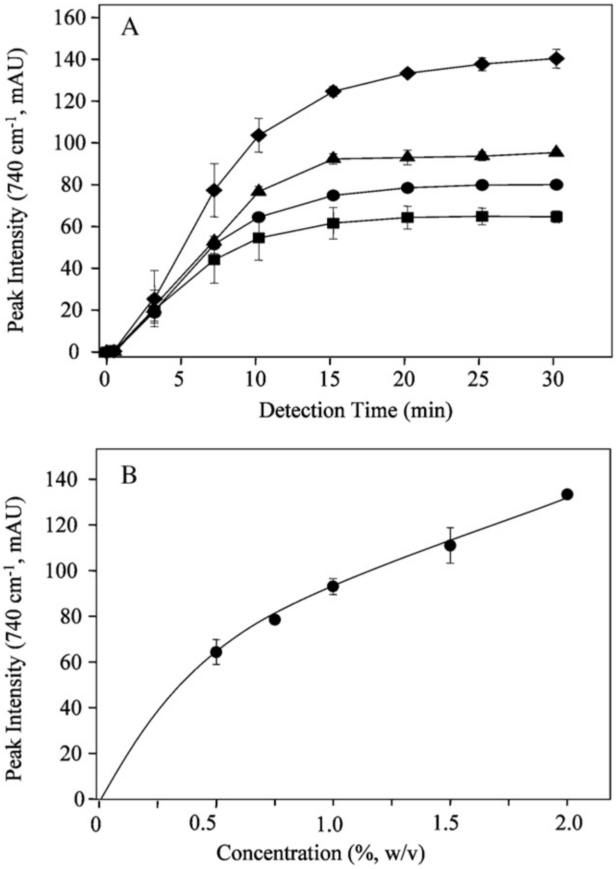

Fig. 6. (A) Detection time profiles of 10 mg/L chlorobenzene by IREs coated with tetra-rhenium metallacycle in concentrations of 0.5% (w/v) (■), 0.75% (w/v) (●), 1.0% (w/v) (▲), and 2.0% (w/v) (◆). (B) Plots of the signals detected with different concentrations of tetra-rhenium metallacycle and the IR signals taken at 20 min.

detection equilibrium grew as the amount of the tetra-rhenium metallacycle coating was increased. For instance, more than 30 min were needed to obtain the maximum signal with a 2.0% (w/v) concentration of coating solution, but only 15 min were required with a concentration of coating solution lower than 1.5% (w/v). This implies that as the thickness of the sensing phase increases, the time required for the analytes to diffuse into the active sites also increase. The relationship between different concentrations of coating solution and detected signals, for a detection time of 30 min, are shown in Fig. 6B, which shows an exponential growth relationship. This indicates that it becomes more difficult for the VOCs to diffuse into the inner layer of metallacycle, in proximity to the evanescent field of the ATR element, as the coating thickness is increased. In terms of sensitivity, a 2% (w/v) is suggested for quantitative purposes, as it provides the largest signal.

3.5. Quantitative aspects

To investigate the detection limits and the linear range of concentrations for the tetra-rhenium metallacycle modified IRE infrared sensor in the analyses of VOCs, each of the detectable VOCs examined above were tested. Because trichloroethylene exhibits weak absorption bands, it was selected and used to dilute the VOCs to reduce variations caused by uncertainty in the injected volume. The VOCs were diluted with trichloroethylene at different concentrations and injected into the sample cell to form different concentrations of chlorobenzene prior to detection. Fig. 7A presents the detection time profiles for different concentrations of chlorobenzene. As the figure indicates, more than 30 min were needed to reach the maximum signal intensity. The delay is clearly due to the time required for the analytes to diffuse into the inner layers of metallacycle. To shorten the time required for analyses, the feasibility of using a non-equilibrium analytical signal in quantitative analysis was assessed by plotting the concentration profiles of chlorobenzene for different detection times. The results are shown in Fig. 7B. The figure shows that the dynamic range is extended if non-equilibrium results are used. On the contrary, a plot of signals under equilibrium shows that, with equilibrium signals, the sensor will be more sensitive toward analytes although the dynamic range will be reduced compared to the use of non-equilibrium sensing. On the basis of three times the noise level, for 30 min of elapsed time, the detection limit for chlorobenzene was around 50 μg/L.

To further examine the effect of interference, chlorobenzene was chosen as the target molecule and samples prepared by mixing chlorobenzene with a second VOC to form a concentration of 10 mg/L for each of the components. These VOCs included acetone, chloroform, ethanol and toluene. To simplify the comparison, recovery was defined here as the ratio value of the intensity of the detected signals of chlorobenzene with second component to that of without second component. The results show that the recoveries in determination of the concentration of chlorobenzene when co-presented with acetone, chloroform, ethanol and toluene were 95.8(±6.6), 95.4(±5.1), 100.1(±3.8), and 99.8(±5.5), respectively. These values indicated that the second component did not inference the analytical signals significantly.

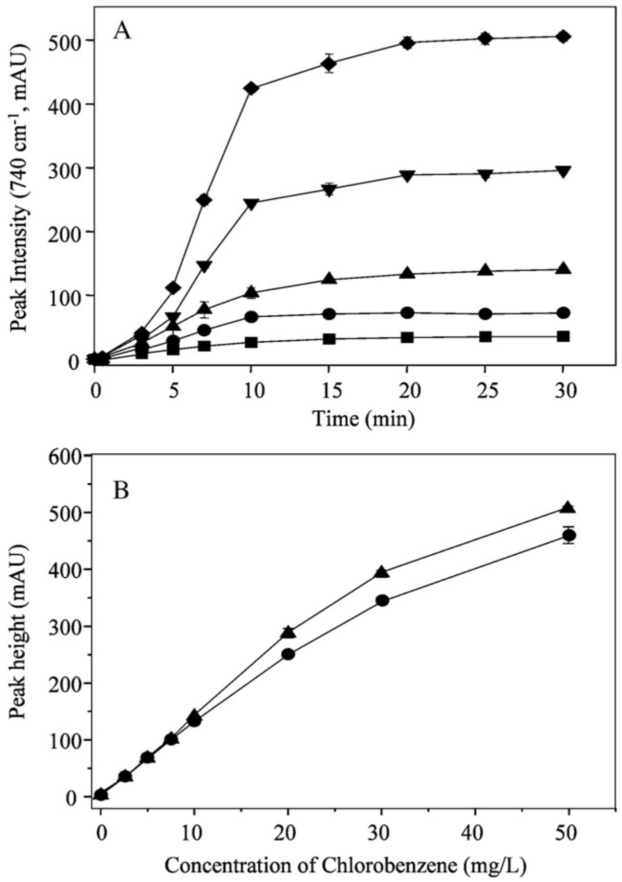

Fig. 7. (A) Detection time profiles of varying injected volumes of chlorobenzene by the rhenium-based metallacycle modified IR sensor. The IRE was treated with 2.0% (w/v) of metallacycle. The concentrations of chlorobenzene were 2.5 (■), 5 (●), 10 (▲), 20 (▼), and 50 mg/L (⧫). (B) Plots of injected amount of chlorobenzene *vs.* detected signals at detection times of 15 (●), and 30 min (▲).

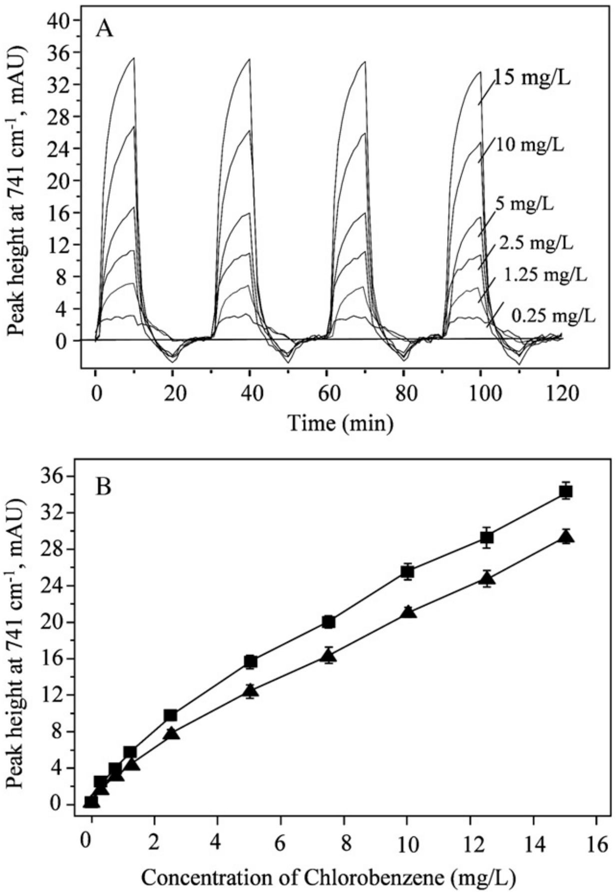

Fig. 8. (A) Detection time profiles in detections of four consecutive injections of different concentrations of chlorobenzene using a flow-cell device. The IRE was treated with 0.5% (w/v) of metallacycle. (B) Plots of concentrations of chlorobenzene *vs.* detected signals at detection times of 5 (▲), and 10 min (■).

3.6. Simplification of detection procedures by a flow-cell device

As can be seen in the response time profiles for static detection system, tetra-rhenium metallacycle sensing phase exhibits fast in responses. This reveals that the determination of VOCs is approachable by a configuration of flow cell. A flow cell device as shown in Fig. 1B was constructed to determine the chlorobenzene in different concentrations. In this device, an electric heating chip was used to heat the IREs to a temperature of 60 °C for increasing the efficiency in regeneration of the sensing phase. A switching valve was located in the inlet of the flow cell to direct either nitrogen or sample gas in a flow rate of 20 mL/min. Samples were prepared by injection certain amount of chlorobenzene in to a 4 L bottle and wait for at least 10 min before carried to the flow cell for detection. After end of the detection, nitrogen gas was directed to the flow cell and heated at same time to regenerate the sensing phase. After 5 min, the heater was switched off and the cell was further purged with nitrogen for 5 min to release the heat before a new injection started. The obtained response profiles are plotted in Fig. 8A for the detection time profiles for 4 consecutive injections. The signals taken at a detection time of 5 and 10 min after injections were plotted against the concentrations of chlorobenzene as plotted in Fig. 8B. By comparing the performances of static detection system as the data shown in Fig. 7, the flow-cell device provided similar performances but the whole detection process was simplified as one analysis can be completed within 20 min.

4. Conclusion

In this work, a new class of neutral rhenium-based metallacycle was successfully synthesized, then used to modify the surface of IREs as infrared chemical sensors, which then were thoroughly tested. This sensing scheme takes advantage of the molecular recognition properties of cavity-containing metallacycles in addition to the abundant molecular information provided by infrared spectroscopy. To optimize the proposed sensing method, the characteristics and the sensing properties of the sensor were examined. The results indicate that tetra-rhenium metallacycle films showed specific affinity toward aromatic compounds, particularly to aromatic compounds with polar functional groups. The detailed studies suggest that the strong interactions between tetra-rhenium metallacycle and aromatic compounds with polar functional groups were the result of both the cavity structure and the crown ether-like recognition sites of metallacycle. Moreover, the optimal amounts of rhenium-based metallacycle coated on the IRE are proportional to the analyte capacity and the resulting analytical signals. Based on the detection time of the profiles collected under optimal conditions, sensing is fast in response and the detection time for volatile aromatic compounds is generally shorter than 20 min. In terms of quantitative analysis, the results indicate that this sensing phase is highly sensitive to aromatic compounds and that the linear range for compounds tested generally extends to 30 mg/L with detection limits *ca.* 30 μg/L.

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