Novel Sensing Technique for Environmentally Toxic NOx Gases
Calixarene-Nitrosonium Complexes

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Introduction

Nitrogen dioxide (NO₂) is a colorless, non-flammable gas with a detectable odor. NO₂ gas is a strong oxidizing agent that reacts in air to form corrosive nitric acid and many toxic organic nitrates. The major man-made source of NO₂ is high temperature fossil fuel burning in vehicles and industries in which emit NOx. NO₂ in the atmosphere then nitric oxide combines with ozone to produce NO₂.

Currently a number of sensing techniques have been developed to detect NO₂ in ppm and ppb levels. Most of the available methods require either harsh or very delicate operating conditions.

In this work we have developed a novel versatile method of detecting NO₂ in sub ppm levels. Different calixarene derivatives have been used.

Calixarene NO⁺ Complexes

The use of simple calix[4]arenes to chemical fixation of NO₂(NO₃)₂⁺[g] is demonstrated in the solid and solution phases.

Experimental Preparation of the plate

Comparison of preparing methods

Soaking was the best way for preparation. Drop methods makes concentration gradient on the plate.

Schematic flow diagram

Sample gases impinging on TLC plate via small nozzle

Response to NO₂

UV Spectrum of calixarene & NO₂

In CHCl₃

Calixarene + NO₂

Typical response to NO₂

Sample gases were exposed for 5 min then purified air was exposed.

What happens to calixarene?

During repeating gas exposure and release process, sensitivity decrease has been observed.

Illuminated LED

LED light which was used for absorbance detection made decompose calixarene.

Light intensity & response

Exposed light power also made difference on the life time.

Conclusion

Soaking was the best way for preparing uniform treated plates.

Limit of detection (LOD) : 0.1 ppmvNO₂, ( 5 min gas sampling, 3 times of noise)
Light acts as a catalyst in the nitration of calixarene.

Long chained calixarene showed lower sensitivity. Blocked calixarene could not release NO⁺ due to high binding affinity.

Chemical approach

Upon exposure to light, calixarene-nitrosonium complexes tends to photo decompose. This is mainly due to nitration of open positions of the phenyl rings in calixarene. To overcome this problem different conformations of calixarene and methyl blocked calixarene derivatives have been used.

Chemical approach for:
1) Improving sensitivity : Long chain
2) Avoiding photo decomposition : Block the reaction site

Long chain developed same color with NO₂. However, blocked the reaction site one developed yellow – brown color.

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