

Novel Pyridinium Luminophores for Optical Ammonia Detection

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Summary:

Ammonia detection is one of the actual problems in food packaging applications. This paper presents the results of the study of optical sensors of ammonia vapor based on novel organic pyridine luminophores modified with acids. Optical, structural properties of luminophores at room temperature were investigated. The sensitivity of the luminophores to ammonia vapor in the 20-700 ppm concentration range was investigated.

Keywords: optical sensors, ammonia, pyridinium luminophores, optical sensors, biogenic amines, food safety, photoluminescence, volatile organic compounds.

Introduction:

Biogenic amines, such as ammonia, detection is one of the actual problems in food packaging applications. Classical methods of food quality control are time consuming, including expensive materials and technics [2]. Optical sensors for the detection of biogenic amines are becoming a real challenge for industrial and food safety applications [1,2]. This is due to their simplicity, low-cost production technology, and ability to operate outside of laboratory conditions. Pyridinium luminophores are promising materials for application in the field of optical sensors, which demonstrate highly intensive photoluminescence with high quantum yield at room temperature. These organic structures could be easily chemically tuned according to industry needs. One of the methods of improving sensitivity to ammonia is the treatment of luminophore with acids. As a base for the future sensors were used 1-(2-(9H-carbazol-9-yl)benzyl)pyridin-1-ium-4-carboxylate (mmd93), chemical structure of luminophore shown in Figure 1, modified with hydrochloric acid (mmd93-HCl) and trifluoroacetic acid (mmd93-TFA).

Experimental part:

Synthesis of mmd93 was performed by following the experimental procedure reported by Ledusk-rasts et al. [3] For modification two portions of mmd93 each were mixed with of HCl and TFA respectively and dried in the furnace overnight. Sensor tests with ammonia vapors were provided in a specially designed chamber.

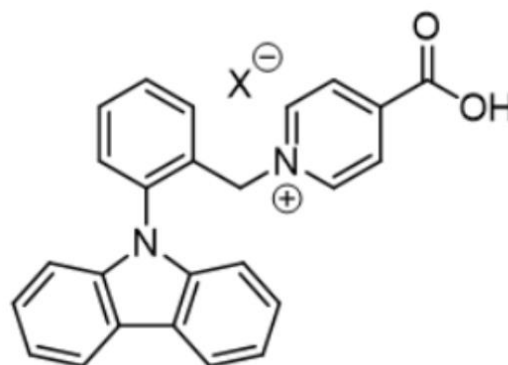


Figure 1. Chemical structure of mmd93 modified with acid.

The chamber ($V_c=7.7$ l) isolated from the environment, equipped with ventilator, sample holder, quartz window, inlet and outlet. The probe consists of precisely measured volume of ammonia saturated vapors ($V_a \ll V_c$) injected inside with a syringe. Photoluminescence (PL) was initiated with portable light source (UV LED, 325 nm, 0.05 mW). During the sensor testing full PL spectra was recorded before and after injection of each probe. Kinetics was recorded for pre-selected wavelengths.

Results and Discussion:

From FT-IR spectroscopy (Figure 2) we can observe changes in spectra for all the samples in $1500 - 750$ cm^{-1} . That could be explained by the interactions between luminophore and introduced acids with formulation of new carboxylic groups. Diffuse reflectance spectroscopy shown red shift of the peak of absorption for modified

with acids mmd93 (Figure 3).

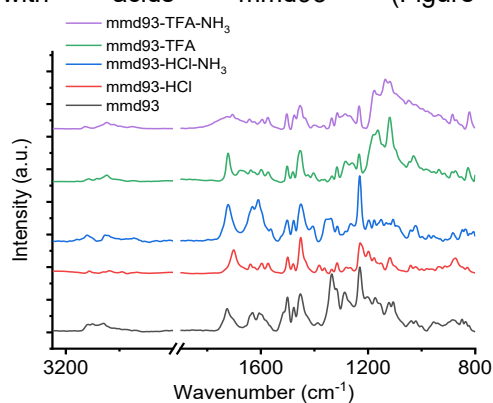


Figure 2. FT-IR of pure and modified mmd93.

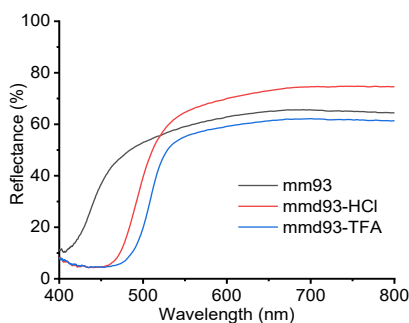


Figure 3. Diffuse reflectance spectroscopy of pure and modified mmd93.

Results of sensor testing of mmd93-HCl and mmd93-TFA against ammonia vapors are presented in Figure 2 and Figure 3 respectively. Intensity of PL decreases for both samples during the experiments upon the interaction of ammonia vapors.

For mmd93-HCl measurements were provided in the range of the concentrations of ammonia vapors between 20 ppm and 200 ppm. For mmd93-TFA sensor testing were performed in the range of concentration 50 – 700 ppm of ammonia vapors.

As we can observe interaction with ammonia vapors for each compound results in different form of kinetic curve and reaction initiates with different vapors concentrations.

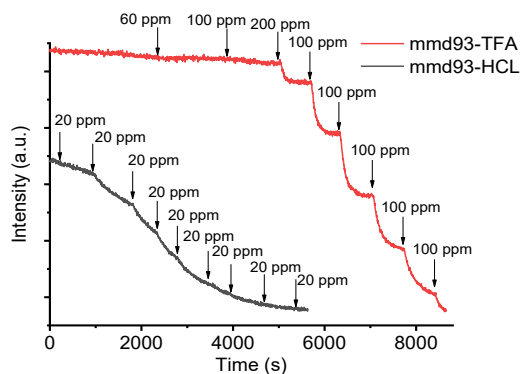


Figure 4. Kinetics of sensor response of modified compounds for ammonia vapors.

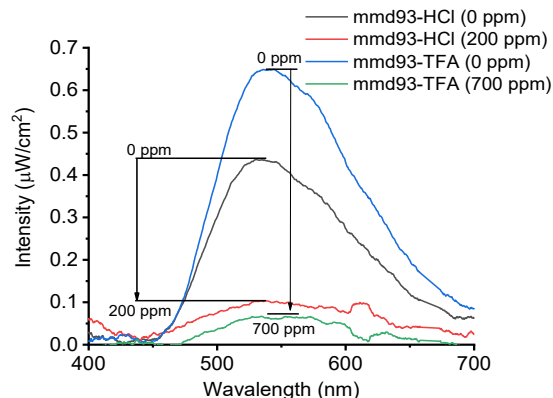


Figure 5. Full spectra of modified compounds before and after interaction with ammonia.

Conclusions:

Investigated compounds show PL response for ammonia. Sensor range, sensor response time calculated for interaction with ammonia vapors. Compounds show promising results for detection of ammonia vapors at room temperature, what is applicable for food packaging applications. Further studies will be provided to optimize the sensor performances (sensitivity, selectivity, limit of detection).

References:

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