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Novel pyridinium luminophores as optical gas sensors for detection of volatile acids

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Summary:
Detection of volatile acids (VA), such as HCl, TFA, etc., in industrial processes and biological reactions is an actual problem. Pyridinium luminophores is a new class of materials with tunable chemical structure and optical properties. Sensor properties of these materials have not been explored yet. This study presents fabrication of pyridinium luminophores and characterization by XRD, FTIR and photoluminescence (PL) spectroscopy. The material, tested PL spectroscopy at room temperature, exhibited outstanding sensitivity towards VA, attributed to its chemical structure. These findings underscore the potential of pyridinium luminophores for effective detection of VA in hazardous environments.

Keywords: Volatile acids, Optical gas sensors, Pyridinium luminophores, Photoluminescence.

Introduction

Volatile acids (VA) such as HCl, TFA, etc., are common by products in industrial processes and biological reactions [1]. Effective and low-cost detection of is crucial for environmental monitoring and human health. Recent approaches show significant progress in VA detection by using resistive sensors [1]. The sensors, constructed from metal oxides, metal alloys and conductive polymers showed high sensitivity and selectivity towards VA at room temperatures [1]. Organic compounds with advanced optical and structure properties are efficient alternatives for VA detection [2]. VA vapors have been detected by metal organic compound (MOF) sensors using photoluminescence spectroscopy at room temperature [2]. Despite the reversible signal, the concentration range of the MOF sensor and optical detection units are to be optimized [2]. Pyridinium luminophores are novel organic semiconductors with high quantum yield, mainly used in light emission diodes [3]. Their unique properties exhibit high potential for photoluminescence gas sensor applications. In the present research we report on novel pyridinium luminophores have been synthesized and studied by X-ray diffraction (XRD), FTIR spectroscopy, and photoluminescence spectroscopy (PL). PL spectroscopy has been used to examine sensor properties of the luminophores to vapors of HCl, TFA and acetic acids at room temperature.

Synthesis of pyridinium luminophores

The luminophores have been prepared as described in [3]. In the final step, the reaction with HCl at 70 ^{0}C has been performed. The precipitated powder was dried in vacuum and analysed by NMR. The structure of the obtained luminophore is shown in Figure 1.

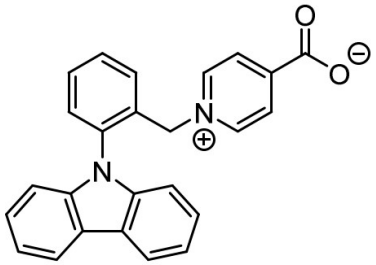

Fig. 1. Chemical structure of pyridinium luminophore.

Gas sensor testing

Gas sensor testing to HCl, TFA and acetic acid was performed in home made gas chamber. The gas chamber (V_c=7.7 l) was equipped with a ventilator, inlet and outlet, sample holder and quartz window. Saturated vapor with precise volume V_s (V_s<<V_c) was injected into the chamber. Photoluminescence (PL) was excited by UV LED (325 nm, 0.05 mW) and the optical sensor signal has been measured by fiber optic spectrometer (Ocean Optics HR2000). During the sensor tests, the full PL spectrum was recorded before and after adsorption equilibrium. Kinetic measurements have been performed at the pre-selected wavelengths.

Results and discussion

Sensor response of the pyridinium luminophore to HCL and TFA is presented in Figure 2 and 3, respectively. The PL intensity of the luminophore decreased upon interaction with acidic vapors. The sensor showed significant response to HCl in the range of 90-360 ppm, whereas sensor range towards TFA vapors was at 350-1400

ppm. Kinetic response to volatile acids was recorded at fixed wavelength of 520 nm (Figure 4). The sensor response was about 250 seconds for HCl and 1000 seconds for TFA.

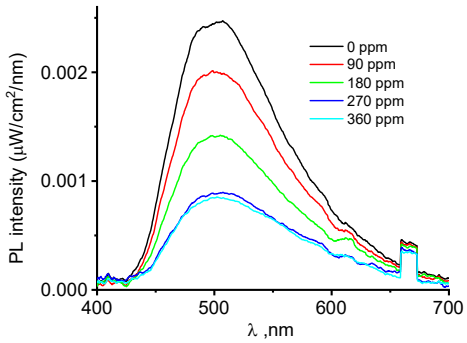

Fig. 2. Sensor response of pyridinium luminophore to HCl vapors measured by photoluminescence spectroscopy

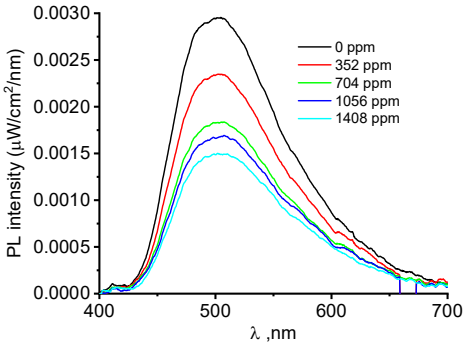

Fig. 3. Sensor response of pyridinium luminophore to TFA vapors measured by photoluminescence spectroscopy

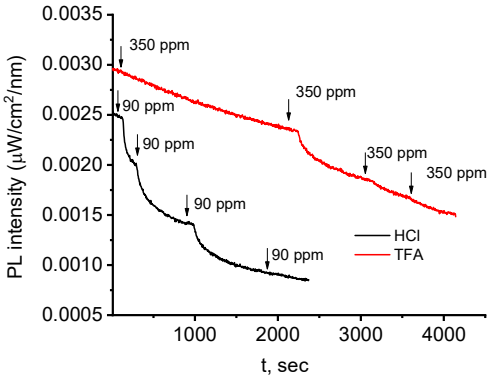

Fig. 4. The Kinetic response of the pyridinium luminophore to HCl and TFA vapors were recorded at fixed wavelength of 520 nm.

FTIR spectra of the pyridinium luminophore before and after are shown in Figure 5. Peak shift from 1630 cm^{-1} to 1703 and 1730 cm^{-1} suggest on protonation of the luminophore and forming of carboxylic groups as result of interaction with volatile acids. The observed changes in the chemical structure of the luminophore depend on the acidic strength of the volatile acids.

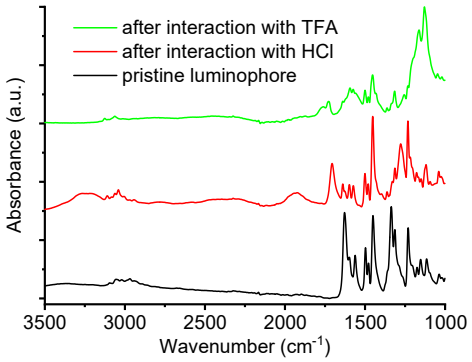

Fig. 5. Sensor response to HCl vapors measured by photoluminescence spectroscopy

Conclusion

The synthesized pyridinium luminophore has shown chemical interaction with volatile acids. Sensor range, senor response time and interaction mechanism were the function of the acidic strength of the volatile acid compounds. This material shows promising behavior for detection of volatile acids at room temperature, what is applicable for environmental and industrial gas sensors. Further studies are finalized to optimize the sensor performances (sensitivity, selectivity, limit of detection).

References

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