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Schiff-base as highly sensitive and reversible chemosensors for HCl gas

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ABSTRACT

Two optochemical sensors based on Schiff-bases doped polymethyl methacrylate (PMMA) films were obtained. The gas sensing behavior of the sensors were investigated with respect to the detection of HCl gas by absorption and fluorescence spectra at room temperature. The detection method is based on the protonation of Schiff-bases by HCl gas. It was found that two sensors exhibited good response, reversibility and stability to HCl gas. The color changes of sensors upon protonation are obvious, which can be observed with naked-eye. The changes of the spectra are likely due to increase in planarity of the molecular framework, which has been confirmed by quantum chemical calculation.

1. Introduction

Hydrogen chloride (HCl) gas is primarily produced by burning of halogenated polymers, incineration of plants, absorption tower of semiconductor factories [1]. Since HCl gas is harmful to the human body, the concentrations of HCl gas are strictly regulated in the workplace [2]. In order to monitor the release of HCl into the environment, an efficient HCl sensor with high sensitivity and reliability is really in demand [1–12]. The numerous analytical methods such as solid electrochemical [9] and amperometric [11], not only require a great deal of samples but also need long time-costing, which is thus not suitable for continuous monitoring. In contrast, the method based on photochemistry offers distinct advantages in terms of sensitivity, selectivity, response time and local observation. Moreover, remote sensing is possible by using optical fibers with a molecular sensor immobilized at the tip [13]. Therefore, considerable efforts are being taken to develop sensitive optochemical sensors for the detection of HCl gas [14,15].

Recently, porphyrin dyes [1,5,7,10,12,16,17] have been widely applied in the detection of HCl gas based on the changes in absorption spectra due to the protonation of the inner nitrogen core of the porphyrin ring [5]. However, the tedious synthesis of porphyrin dyes with low yields confined their further development as sensors. In the other hand, most of Schiff-bases are readily obtained by relatively simple synthesis procedures, which provide various structure modifications [18–25]. The carbon–nitrogen double bond unit of Schiff-bases can be also protonated and hence are sensitive to acid. Protonation of Schiff-bases in acidic aqueous system results generally in the hydrolysis [26], Schiff-bases doped with polymer were thus used in response to hydrogen ion (H^+) in order to avoid the hydrolysis. Derinkuyu et al. reported spectral characterization of two Schiff-bases in solid matrices of polyvinyl chloride (PVC) and ethyl cellulose as pH sensors, respectively [27,28]. Hazneci et al. introduced novel Schiff-bases in plasticized PVC matrices as optical pH sensors [29]. Although the sensors based on Schiff-bases have been successfully applied to detect H^+ in aqueous solution, their application in the detection of HCl gas are rarely reported.

Based on above considerations, two Schiff-bases, N4,N4′-bis((4-(diphenylamino)phenyl)methylene)-4,4′-benzenediamine (**1**) and N4,N4′-bis((4-(diphenylamino)phenyl)methylene)-(1,1′-biphenyl)-4,4′-diamine (**2**) were synthesized. Triphenylamine (TPA) segment was introduced into the target compounds to improve sensitivity of chemosensors due to its excellent fluorescence properties [30–36]. Two optochemical sensors have been successfully fabricated by spin-coating of dichloromethane (CH_2Cl_2) solutions containing **1** or **2** doped with polymethyl methacrylate (PMMA). In the presence of gaseous HCl, the red-shift of the absorption maxima of two sensors was both observed and accompanied with the enhanced luminescence, which are attributed to the increase of planarity of the molecular framework due to the protonation of nitrogen of carbon–nitrogen double bond

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unit [28,29]. This conclusion was confirmed by quantum chemical calculations. The color changes and luminescence switching of solid-state sensors can be reversed in the presence of gaseous ammonia. The results show that both are the solid-state sensors of HCl gas with fast recovery and high sensitivity.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals were of A.R. grade, and all solvents used were purified by standard methods. Nitrogen gas was purchased from Juyang Industrial Gases Ltd. (Changchun, China). HCl gas was prepared by reaction of concentrated sulfuric acid and sodium chloride in the laboratory.

IR-spectra were measured on Shimaszu IR prestige-21 using KBr pellets in the range of 450–4000 cm^{-1}. ^{1}H-NMR spectra were recorded on Bruker AV-300 MHz spectrometer in $CDCl_3$ solution with TMS as internal standard. Fluorescence measurements were performed on a Shimaszu RF-5301PC spectrophotometer. Absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The thickness of coating films were determined by the bruker D8 discover XRD. Single crystal X-ray diffraction analysis was performed on a Bruker Smart apex CCD diffractometer. The structures were solved by the directed methods and refined by fullmatrix least-squares on F^2 using the SHELXTL crystallographic software package [37]. The organic hydrogen atoms were generated geometry. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 871587 (for **1**) and 871588 (for **2**).

The geometric and electronic structures of **1** and **2** were calculated at DFT level using the B3LYP [38,39] functional and 6-31G basis set as implemented in Gaussian03 programs [40]. Electronic ground states of **1** and **2** were calculated based on the geometries obtained from their single-crystal structures.

2.2. Synthesis of compounds *1* and *2*

Synthesis of the target compounds **1** and **2** were described in Scheme 1. **1** and **2** were synthesized by condensation between 4-formyltriphenylamine and 1,4-diaminobenzene or benzidine with high yield, according to the literature procedure [41]. All compounds were characterized by ^{1}H-NMR and FT-IR techniques.

Compound **1** was a light-yellow solid, yield 90%. M.P.: 193.5–195.0 °C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ (TMS, ppm) 8.41 (s, 2H), 7.74 (d, J = 8.6 Hz, 4H), 7.30 (t, J = 7.8 Hz, 8H), 7.24 (s, 4H), 7.20–7.04 (m, 16H). FT-IR (KBr), v/cm^{-1}: 1617 (CH=N), 1587, 1508, 1489 (C=C, benzene ring), 1269 (tertiary amine), 883.4, 756.1, 694.4 (C—H aromatic).

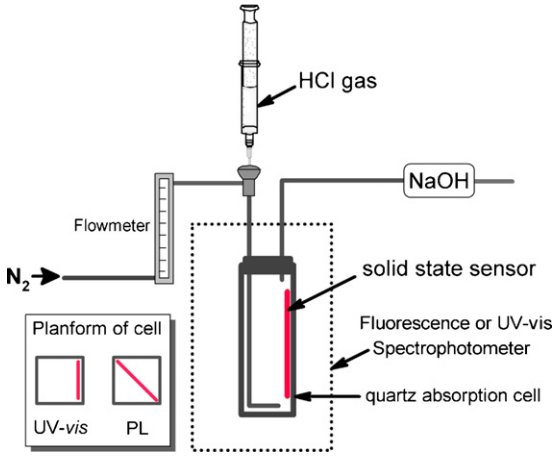


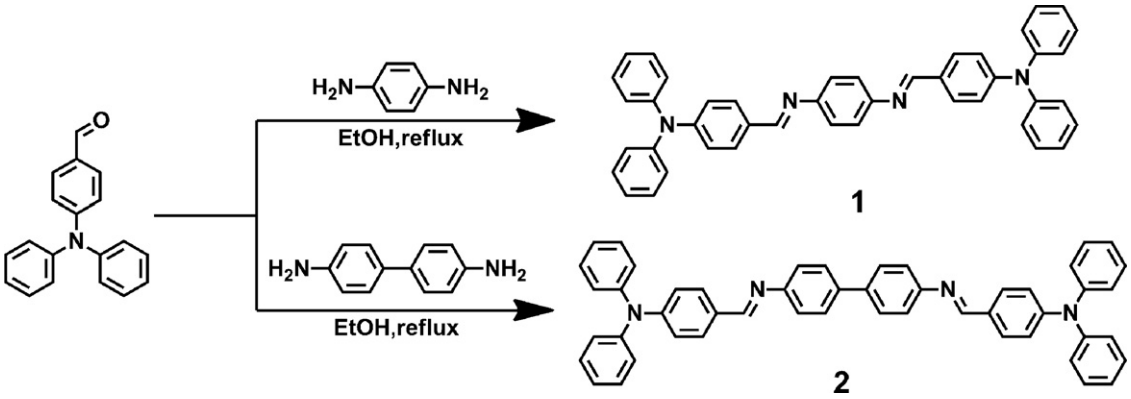
Fig. 1. Apparatus for HCl gas detection.

Compound **2** was a pale-yellow solid, yield 92%. M.P.: 238.7–240.1 °C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ (TMS, ppm) 8.43 (s, 2H), 7.76 (d, J = 8.7 Hz, 4H), 7.64 (d, J = 8.4 Hz, 4H), 7.43–7.26 (m, 12H), 7.24–7.01 (m, 16H). FT-IR (KBr), v/cm^{-1}: 1614 (CH=N), 1585, 1504, 1489 (C=C, benzene ring), 1285 (tertiary amine), 831.3, 752.2, 696.3 (C—H aromatic).

2.3. Preparation of the sensors and sensing procedure

Sensors **1** and **2** were spin-coated from CH_2Cl_2 solution with PMMA (10 wt%). Residual solvent was removed by heating the films in the vacuum. Before preparing the thin films, quartz glass slides were thoroughly washed with double stilled water and acetone, and then dried under argon atmosphere. All the measurements were carried out at room temperature. The thickness of the coating films was approximately 5 μm.

The homemade flow cell set up was used to detect HCl gas according to the literatures [5,8] as shown in Fig. 1. Flowmeter was used to monitor the flow rate of nitrogen gas (10 mL min^{-1}). Gaseous HCl with various concentrations was obtained by injecting a certain volume of HCl gas, with an airtight syringe into the sealed testing chamber where the sensor was placed. Sensing properties of the sensors exposing to HCl gas were monitored by the variation of fluorescence intensity and absorbance spectrum. The sensors were recovered the initial state by injecting dilute ammonia vapor.



Scheme 1. Synthetic pathway of compounds **1** and **2**.