

Abnormal effect in hydrogen gas sensors based upon pyridylimidazonaphthalene

Yuichiro Tsukada, Keita Hirao, Jin Mizuguchi; Graduate School of Engineering Yokohama National University; 79-5 Tokiwadai, Hodogaya-ku, 240-8501, Yokohama, Japan

Abstract

Organic pigments were once extensively investigated as photoconductors for the electrophotographic photoreceptor. Nowadays, they play an important role as colorants for color copies as well as materials for optical discs, electroluminescence, FET etc. Here, we report another novel application of organic pigments for H_2 gas sensors. We have previously developed a H_2 gas sensor that utilizes a high proton affinity of diketodipyridylpyrrolopyrrole. We extended our system to other pigments such as perylene-imides with pyridyl rings. Then, we encountered an anomalous effect in pyridyl-imidazopyrrole (PIP) that the sensor current increases even after shut-off of H_2 . In the present investigation, a similar compound called pyridyl-imidazonaphthalene (PIN) has been tackled in order to systematically interpret the anomalous effect in PIP and PIN. As a result, the two N atoms in the pyridylimidazo group are responsible for the effect. Furthermore, PIP is found to be quite inert to H_2O and H_2 . This makes a string difference between PIN and PIP which is closely linked to the sensitivity of the H_2 sensor.

1. Introduction

In the course of our investigation on the electronic structure of diketopyrrolopyrrole pigments, we have accidentally found that dipyrrolyldiketopyrrolopyrrole (DPPP: Fig. 1 (a)) possesses a high proton affinity due to the N atoms of the pyridyl rings [1]. Furthermore, protonation at the N site brings about a drastic color change from vivid red to dull red, accompanied by a remarkable reduction of the electrical resistivity by five orders of magnitude. Because of this, we have developed a high-performance H_2 sensors of the type of proton acceptors [2, 3]. Further attempt was also made to extend our system to other pigments with pyridyl rings such as perylene-imides [4] and phthalocyanines [5]. These exhibit an even better performance than DPPP.

Then, we encountered pyridyl-imidazopyrrole (abbreviated to PIP: Fig. 1(b)) which exhibits an abnormal effect that the sensor current increases even after shut-off of H_2 [6]. This motivated us to test a structurally similar compound called pyridyl-imidazonaphthalene (i.e. the title compound abbreviated to PIN: Fig. 1(c)) since these are chemically related. PIP is found to also exhibit the abnormal behavior. So we believed firmly that the pyridyl-imidazo group at the periphery must be responsible for the anomalous effect and that the two N sites (N1: outer N; N2: inner N) are involved in the protonation. Our previous report deals with the anomalous mechanism of PIP [6]. Our goal of the present investigation is to further clarify the anomalous mechanism of PIN by comparing electronic and optical properties of PIN with those of PIP.

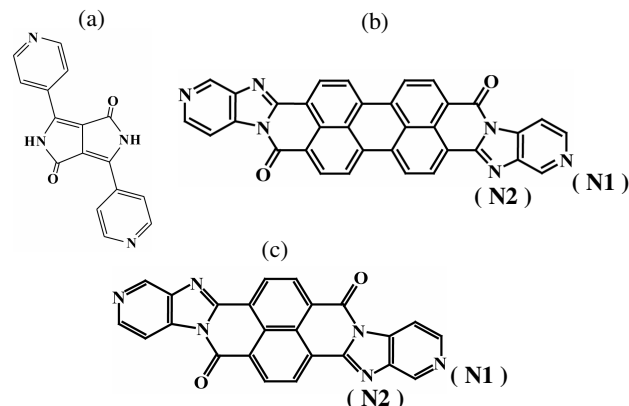


Fig. 1. Molecular conformation: (a) DPPP, (b) PIP and (c) PIN

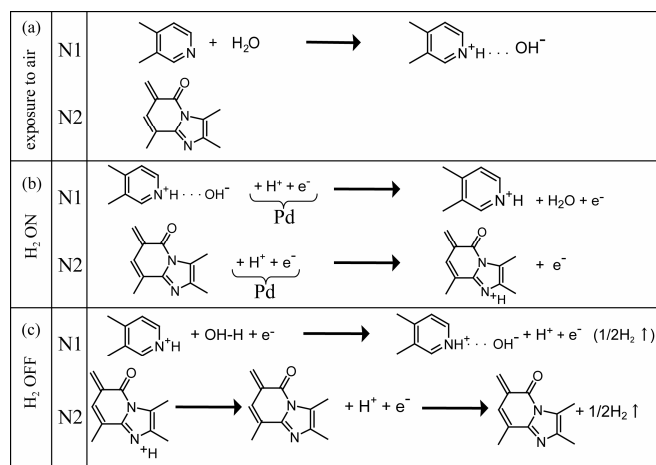


Fig. 2. Proposed mechanism for the H_2 sensor characteristics for PIP.

The tentative interpretation of the anomalous effect in PIP will be briefly outlined as shown in Fig. 2 [6]. The whole process is composed of three steps: step (a) (initial state), step (b) (H_2 introduction) and step (c) (H_2 shut-off). In the initial state, as soon as the sensor is taken out of the vacuum chamber, water molecule in moisture protonates immediately at the N1 site because the electron density is higher at N1 than N2; whereas the N2 site remains intact. This protonation causes the color change of the sensor from blue to violet. Then, upon introduction of H_2 , the protons dissociated from H_2 due to Pd ($1/2H_2 \rightarrow H^+ + e^-$) attack both N1 and N2 sites to release electrons which contribute to the sensor current. Then, the abnormal current behavior occurs when H_2 is off. That is, the sensor current increases for a while and then decreases to the initial state. The increase in current (i.e. abnormal behavior) even after shut-off of H_2 is brought about by the formation of protons at the N1 site which also contribute to the

current until the recombination takes place with an electron to form a hydrogen molecule. The decay process at the N2 site proceeds in an ordinary way: release of a proton to recombine with an electron, ending up with the formation of $1/2\text{H}_2$.

2. Experiment

Synthesis and purification

PIN was synthesized by reaction of 3,4-diaminopyridine with naphthalene tetracarboxylic acid dianhydride at 120°C in phenol for 5 hours. The product was then purified 3 times by sublimation, using a five-zone furnace (Fig. 3).

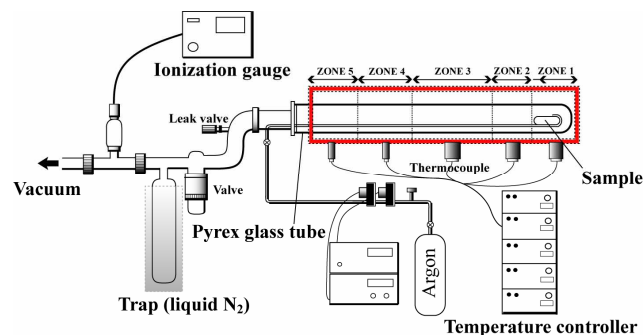


Fig. 3. Sublimation apparatus for purification of

Fabrication of the PIN-sensor

Structure of the sensor is shown in Fig. 4. The interdigital electrodes made of ITO (indium-tin-oxide) were prepared by photolithographic technique. Then, Pd was sputtered directly onto the electrodes in such a way as to form islands of Pd so as to avoid Pd-Pd contacts (about 3 \AA). After that, a thin layer of PIN was applied by vacuum evaporation (about 500 \AA).

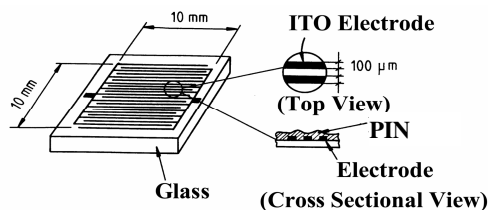


Fig. 4. Structure of the H_2 sensor.

MO calculations

Semi-empirical MO calculations were performed using a CAChe ver. 3.2 program package which includes MOPAC and ZINDO programs. The geometries were optimized by MOPAC AM1 Hamiltonian. The charge densities of the N atoms were calculated. Spectroscopic calculations were made for the initial, mono-, di-, tri- and tetra-protonated states by the INDO/S Hamiltonian.

UV-visible and IR absorption spectra

UV-visible spectra of the H_2 sensor were recorded on a UV-2400PC spectrophotometer (Shimadzu).

The sample for measurements of IR spectra was prepared in the following way. Pd was sputtered on a KBr substrate (thickness: about 3 \AA), followed by evaporation of PIN under vacuum to the thickness of about 3000 \AA .

3. Results and discussion

- Similarity and dissimilarity between PIN and PIP -

3.1 Build-up and build-down of the H_2 PIN-Sensor

Fig. 5 the response curves for two kinds of samples before and after H_2 : sample 1 is the sample as prepared while sample 2 is the one exposed to air for six days. Both samples show the anomalous effect that the sensor current increases even after shut-off of H_2 for a while and then comes back to the initial state (see step (b) in Fig. 2). It is remarkable to note that the build-up current of sample 2 is about 7 times larger than that of sample 1 and that the current increase after shut-off of H_2 is higher in each sample in proportional to the build-up current.

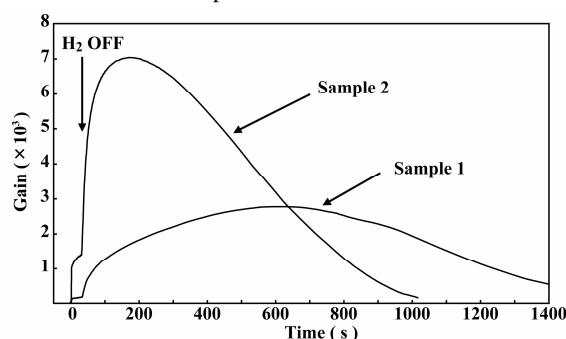
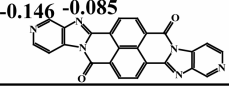
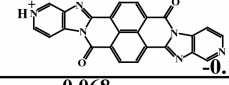
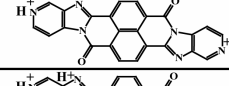
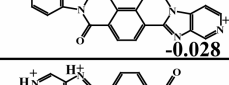
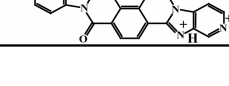


Fig. 5. Response curve of the PIN-based H_2 sensors:

3.2 MO calculations

MO calculations have been carried out in order to gain more insight into the charge density of each atom as well as optical absorption bands. Tables 1 and 2 summarize the result for the charge density of the N atoms and the absorption bands in the initial and protonated states. In the initial state, the electron density is much higher at N1 than at N2, indicating that the first protonation is expected to occur at the N1 site. Protonation at N1 on one side reduces slightly the electron density ($-0.146 \rightarrow -0.138$). Further protonation on both sides of N1 gives a density of -0.068 at the N2 site.

Table 1 Charge density of the N atoms in the initial and variously protonated states.

	Density of the N atoms	Heat of formation (kcal/mol)
Initial state	 -0.146 -0.085	167.2
Protonation 1 (N1 : one side)	 -0.138 -0.146	316.0
Protonation 2 (N1 : both sides)	 -0.068 -0.138	499.3
Protonation 3 (N2 : one side)	 -0.028 -0.068	768.4
Protonation 4 (N2 : both sides)	 0.028 -0.028	1088.3

It should be noted that the absorption band changes remarkably, depending on the extent of protonation. Protonation on one side of N¹ induces a bathochromic shift (416.1 → 480.3 nm); whereas the absorption band is displaced toward shorter wavelengths on protonation on both sides of N¹ (480.3 → 373.5 nm). Further protonation on both sides of N² induces a bathochromic shift again (373.5 → 405.8 nm).

With these results in mind, we will look at the absorption spectra below.

Table 2 Calculated absorption bands and their oscillator strength for the initial and variously protonated states.

	Wavelength (nm)	Ocs. strength (<i>f</i>)
Initial state	416.1	1.28
Protonation 1 (N1 : one side)	480.3	0.78
Protonation 2 (N1 : both sides)	373.5	1.40
Protonation 3 (N2 : one side)	458.7	0.82
Protonation 4 (N2 : both sides)	405.8	1.29

3.3 UV-visible spectra

Fig. 6 shows a series of absorption spectra of the H₂ sensor as prepared, as a function of exposure time of H₂. The absorption spectra change very little and quite slowly. This indicates that PIN is quite inert to protonation, although the electron density is relatively high at the N1 site (Table 1). Nevertheless, the absorption maximum is slightly shifted toward longer wavelengths, accompanied by an isosbestic point at 515 nm. This agrees with the result of MO calculations (Table 2). The existence of the isosbestic point indicates that the spectral change is reversible. In fact, the initial spectrum denoted by “as evaporated” appears after shut-off of H₂. On the other hand, in PIP-based sensor, the corresponding experiment could not be carried out, because the protonation at the N1 site occurs immediately when the sensor was taken out of the vacuum chamber.

The acceleration test by means of saturated water-vapor (instead of water moisture in air) brought about a rapid spectral change as shown in Fig. 7. This protonated sample at N1 corresponds nearly to the sensor that was allowed to stand for six days (see Fig. 5). Because of the water vapor, the absorption maximum is hypsochromically shifted: step (a) in Fig. 2. Then, H₂ exposure for four minutes displaces the absorption band toward longer wavelengths: step (b) in Fig. 2. After 10 minutes of the shut-off of H₂, the spectrum came back again to the initial state (step (a) in Fig. 2). All spectral shifts are in good agreement with the spectroscopic results of MO calculations (Table 2).

In summary, PIN is found to be quite inert against H₂O and H₂, while the reverse is the case in PIP, although no significant difference in electron density is recognized between PIN and PIP. The reason is not known for certain. Once PIN is protonated at the N1 site by H₂O (step (a) in Fig. 2), the PIN sensor becomes suddenly more sensitive to H, resulting in a larger abnormal effect (Fig.5).

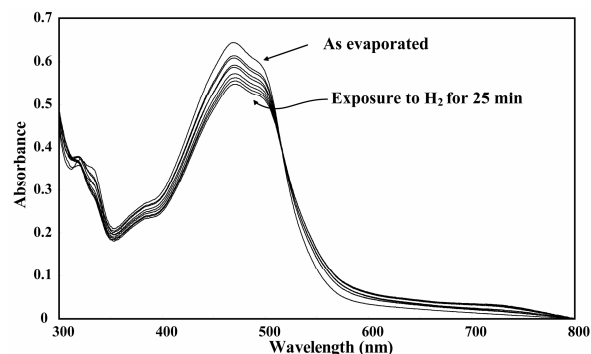


Fig. 6. Spectral change in PIN-based H₂ sensors as evaporated, upon exposure to H₂.

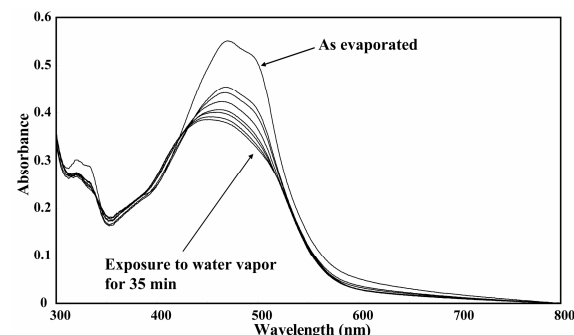


Fig. 7. Spectral change in PIN-based sensors as evaporated, upon exposure to water vapor.

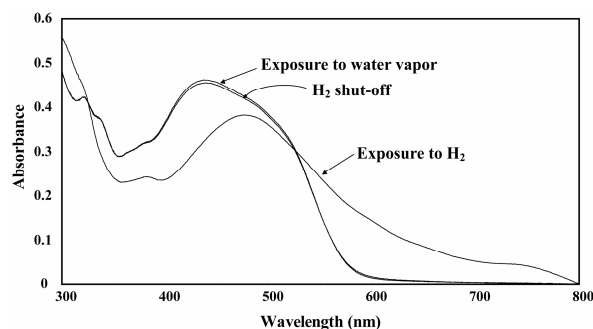


Fig. 8. Spectral change in PIN-based H₂ sensors: exposure to water vapor, exposure to H₂ and shut-off of H₂.

3.4 IR spectra

Step (a) in Fig. 2 is the water-uptake process at N1 in the form of protonation. This process caused by water vapor can be clearly seen in UV/VIS and IR spectra shown in Fig. 7 and 9, respectively. Fig. 7 shows the spectral shift with the elapse of time. As judged from Table 2, protonation takes place at both N1 and N2, because the both protonation brings about a hypsochromic shift. As the protonation due to water vapor proceeds, the broad OH stretching band around 3000-3600 cm⁻¹ grows up, indicating that step (a) in Fig.2 prevails in the sensor.

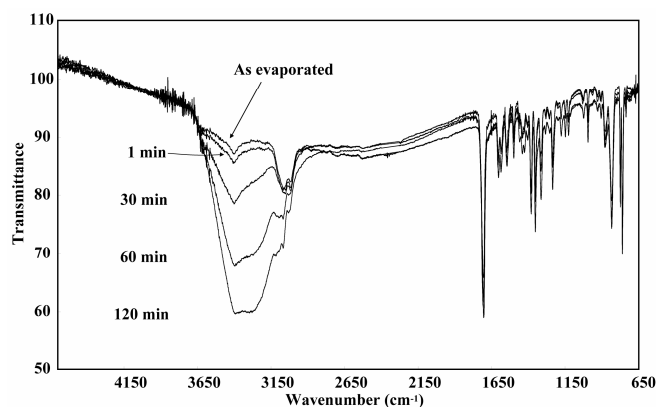


Fig. 9. IR spectral change in PIN-based H_2 sensors upon exposure to water vapor.

4. Conclusions

PIN-based H_2 sensors have been characterized from the standpoint of the anomalous effect observed in PIP. The conclusions drawn from the present investigation can be summarized as follows.

1. PIN-based H_2 sensors exhibit the same anomalous effect as observed in PIP. Two protonation sites in pyridylimidazo group (N1 & N2) are responsible for the effect.
2. The sensitivity of the PIN-based H_2 sensor depends greatly on the extent of the protonation at N1. The more the N1 site is protonated by H_2O , the more the sensitivity increases.
3. PIN is quite inert to H_2O and H_2 . This makes a string difference between PIN and PIP which is closely linked to the sensitivity of the H_2 sensor. However, the reason remains unclarified.

References

- [1] J. Mizuguchi: Solution and solid state properties of 1,4-diketo-3,6-bis-(4'-pyridyl)-pyrrolo-[3,4-c]-pyrrole on protonation and deprotonation, *Ber. Bunsenges. Phys. Chem.* **97**, 684-693 (1993).
- [2] H. Takahashi and J. Mizuguchi: Hydrogen gas sensor utilizing a high proton affinity of pyrrolopyrrole derivatives, *J. Electrochem. Soc.* **152**, H69-H73 (2005).
- [3] H. Takahashi and J. Mizuguchi: Carrier generation and carrier determination in dipyridyldiketopyrrolopyrrole-based H_2 gas sensors, *J. Appl. Phys.* **100**, 034908 (2006).
- [4] K. Sato, K. Hino, H. Takahashi and J. Mizuguchi: Hydrogen gas sensor based upon perylene-imide derivatives, *IJISTA Int. J. Intell. Sys. Technol. Appl.* **3**, 52-62 (2007).
- [5] T. Hoki, H. Takahashi, S. Suzuki, and J. Mizuguchi: Hydrogen Gas Sensor based upon proton acceptors integrated in Copper-tetra-2,3-pyridinoporphyradine, *IEEE Sensors J.* (2007) in press.
- [6] K. Hirao, Y. Tsukada, J. Mizuguchi: Anomalous phenomenon in pyridyl-imidazoperylene H_2 gas sensor, 2007 NIP 23.

Author Biography

Yuichiro Tsukada received his Bachelor of Engineering from Yokohama National University in 2006. He is currently in the graduate course for applied physics at the same university. His research interest includes structure analysis of organic pigments and their electronic applications. E-mail: d06gd223@ynu.ac.jp.