

A Vapochromic Photodiode

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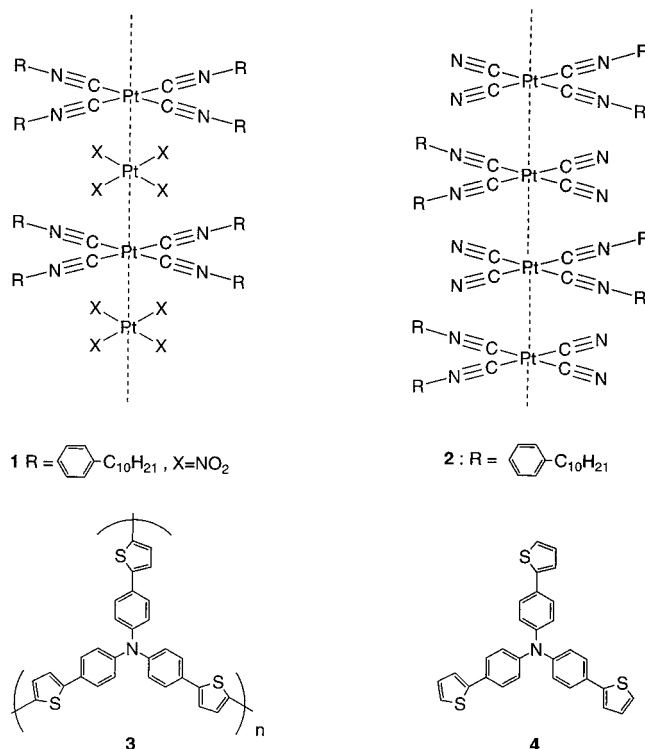
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Recently, we have reported on the vapochromic behavior of certain stacked platinum complexes such as **1** (Chart 1), which have long alkyl chains as part of the ligands.¹ Films of these compounds rapidly absorb organic vapors and this produces pronounced and reversible shifts in the absorption and emission spectra. This unusual effect, that seems to rely on insertion of the small molecules between the stacks, is of interest for remote sensing. Recently, we expanded this idea and developed a new type of sensor technology, a "vapochromic LED".² A sandwich LED³ was prepared using compound **1** that gave electroluminescence from this platinum compound. Exposure of the device to an organic vapor sharply changed the wavelength of electroluminescence, providing a new method for remote vapochromic sensing which does not require a light source.

Here we describe a vapochromic photodiode based on chemical and electrical effects related to those involved in the LED. Organic and polymer photodiodes have been built using materials such as poly(3-alkylthiophene)s, oligothiophenes, and C₆₀. These diodes give photocurrents corresponding to the absorption of light by the molecular materials. They are of interest because they can give wavelength selectivity and quantum efficiencies of more than 10% electron/photon under modest reverse bias.⁴ To our knowledge a photodiode which can detect the arrival of organic vapors has not been described. Its development required an electrode transparent to the incident light, an appropriate vapochromic material, a second molecular layer that formed a rectifying junction with the emitter layer, and a second electrode that would permit vapor to reach the molecular materials.

Bis(cyanide)bis(*p*-dodecylphenylisocyanide)platinum(II) (**2**)^{5,6} was chosen as the stacked platinum complex because it forms good films by spin casting and it exhibits a large color change in response to organic vapors.

Chart 1



The color of the film cast from chloroform solution was yellow (λ_{\max} 400 nm). Exposure of the film to acetone vapor changed the color to reddish-purple (λ_{\max} 560 nm). This reddish-purple color was stable for several months under ambient laboratory conditions, but could be switched back to yellow by exposure to chloroform or dichloromethane vapor. Devices were prepared by spin casting **2** from chloroform solution onto conducting indium–tin oxide (ITO) coated glass, followed by vapor deposition of aluminum. These devices, like single layer devices formed from **1**,² were very resistive, unstable, and did not show rectification.

Recently, we have shown that electrochemical oligomerized tris(4-(2-thienyl)phenyl)amine (**3**) can be used as a hole transport layer to make a two-layer device.² Because the layer of **3** is insoluble in solvents such as chloroform or acetone, it was possible to spin cast a layer of **2** on top of **3** without layer interdiffusion. The two-layer device ITO/**3**/**2**/Al was, therefore, prepared by anodically oxidizing tris(*p*-thienylphenyl)amine (**4**) in acetonitrile, lithium perchlorate providing the oxidized form of **3**, and then electrochemically reducing it to form the neutral **3** (200 nm). After drying, a layer of **2** (250 nm) was spin cast from chloroform on top of **3**, and then aluminum (150 nm) was vapor deposited through a mask on to the layer of **2**. To

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(6) **2** was prepared by a melt method.⁵ Tetrakis(*p*-decylphenylisocyanide)platinum tetracyanoplatinate^{1b} (1.785 g, 1.20 mmol) was placed in a flask and left under an argon atmosphere. As the deep blue sample was slowly heated to 165 °C, the solid melted, forming a reddish brown liquid. Upon cooling, the liquid solidified. It was extracted from the flask with dichloromethane and purified by column chromatography with 17:3 dichloromethane:ethyl acetate (1.526 g, 2.08 mmol, 87% yield). The purified product gave appropriate combustion analysis and spectroscopic data.⁵

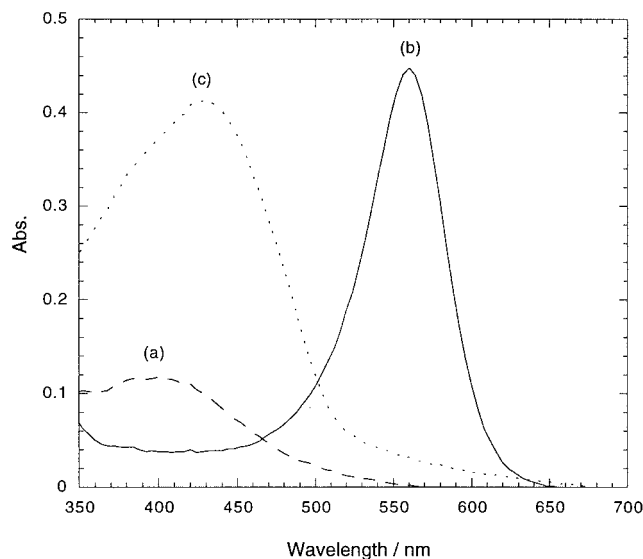


Figure 1. Absorption spectra of **2** (a) before and (b) after exposure to acetone vapor, and (c) **3**.

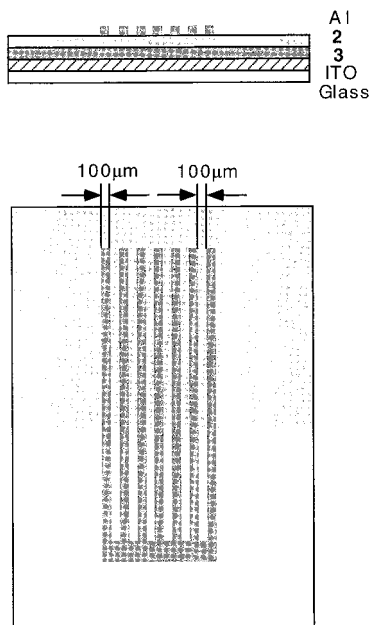


Figure 2. Schematic illustration of the vapochromic *p-n* junction photodiode.

ensure a quick response to the vapor, the aluminum electrode was fabricated as fingers spaced apart by 0.1 mm (Figure 2).

The device ITO/**3**/**2**/Al gave rectification (rectification ratio 100 at ± 5 V) of the current favoring electron flow from Al through the molecular layers to ITO. For photocurrent action spectra a 450 W Xe lamp was used, and the photocurrent was normalized to account for the variation of lamp output with wavelength. A calibrated silicon photodiode was used to measure light intensities. The photocurrent action spectrum of the device ITO/**3**/**2**/Al has a broad peak between 400 and 500 nm (Figure 3a). Exposure to argon saturated with acetone vapor gave a shifted action spectrum (Figure 3b) (λ_{\max} 560 nm) corresponding to the shifted absorption spectrum of **2** (Figure 1b). This spectrum was stable in air in the absence of acetone vapor. Exposure of the device to chloroform vapor in argon (or air) caused the spectrum

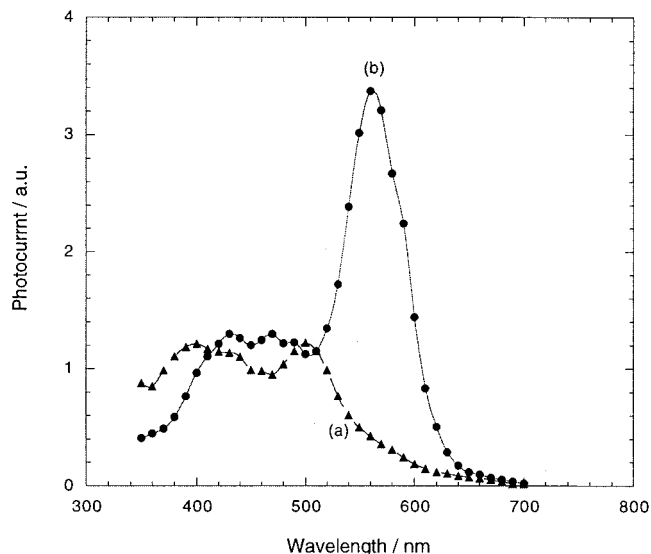


Figure 3. Action spectra for ITO/**3**/**2**/Al cell (a) before and (b) after exposure to acetone vapor. The action spectra were taken by illumination from the ITO side under application of 2 V reverse bias.

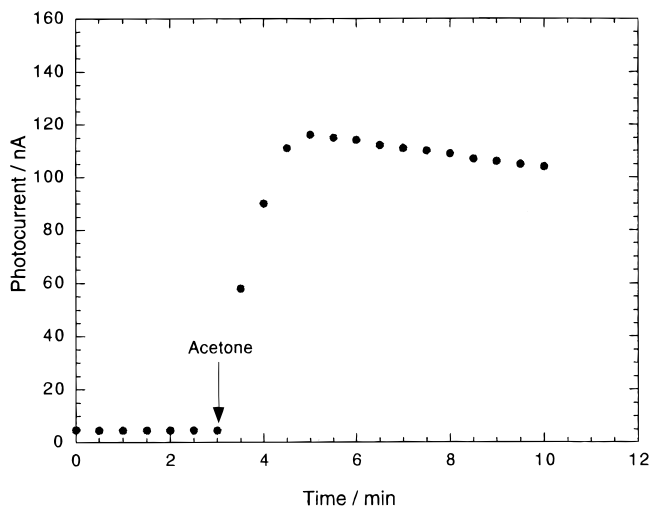


Figure 4. Time dependence of the photocurrent for ITO/**3**/**2**/Al cell illuminated with 560 nm light.

to revert to the original. The shapes of these spectra are independent of light intensity. Illuminated through ITO with 560 nm light (1.0 mW cm^{-2}) the quantum efficiency (electron/photon of absorbed light) of the device was 0.03% at 0 V and 16.5% at 20 V reverse bias. We note that **2** is visibly photoluminescent and so at low bias voltages emission of light can effectively compete with charge separation and photocurrent generation.

The known instability of polymer-based electrooptical devices during operation in air is not such a severe problem for sensors. As a sensor the device only needs to be pulsed occasionally to check for the arrival of the vapor of interest and so operating times can be quite short. In the present case the photocurrent decayed 40% during continuous operation in air. When pulsed the response was much more stable and this allowed us to measure the time dependence of switching. The photocurrent for the ITO/**3**/**2**/Al cell illuminated with 2 s pulses of 560 nm light is shown in Figure 4. When acetone vapor in argon was introduced above the device,

the photocurrent increased more than 10 times in 2 min. This response time is much faster than that for our previously reported vapochromic LED. This seems to be a result of the use of the microelectrode array, instead of relying on the slower diffusion through a porous aluminum layer.

Of interest in terms of mechanism is the action spectrum between 400 and 500 nm (Figure 3), which does not correspond closely with the absorption spectra of either **2** or **3** (Figure 1). To understand this difference we prepared a device with a thicker layer of **3**. The efficiency of this device was smaller at all wavelengths, but especially between 350 and 460 nm. The weaker action spectrum between 500 and 700 nm still followed the absorption spectrum of **2**. These effects appear to result because the active interface is that between **2** and **3** and because **3** acts as an optical filter.⁷ If the ITO/**3**

interface is not active, then the thicker layer of **3** only acts to attenuate the light reaching the region near the active **3/2** interface. A p-n junction is formed at the **3/2** interface and the organic layers, especially **2**, absorb light and give charge separation near this interface.

These preliminary results demonstrate a new class of gas sensors that report the arrival of organic vapors by a change in photocurrent. In one sense these photodiodes are like vapochromic absorption sensors without the requirement for a separate detector of the absorbed light. Since different platinum complexes and/or organic vapors will elicit different optical responses, a variety of chemicals can be detected and there are many opportunities for improving and fine-tuning device performance.

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