A Vapochromic LED

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Received October 20, 1997
Revised Manuscript Received December 2, 1997

Recent reports from this laboratory have enucleated and explained the unusual “vapochromic” changes in absorption and emission spectra that result when certain stacked platinum complexes are exposed to organic vapors.[1] A typical experiment involves a solution, crystal, or solid film of material, such as tetrakis(*p*-decylphenylisocyano)platinum tetracyanoplatinate (**1**), that forms stacks of alternating cations and anions with strong interplatinum interactions. These salts exhibit an intense absorption band in the visible region. Exposing the stacks to small molecule vapors, such as acetone or chloroform, leads to sorption of the vapor molecules in the free volume between the stacks, and produces shifts in the absorption and emission spectra. These “vapochromic” or “vapoluminescent” changes are usually reversible so that the original spectrum is regained quickly after the vapor is removed. Such an effect has obvious application for sensor technology. It occurred to us that a new type of sensor could be devised in which the device could report the arrival of the vapor by incorporating the material into a light emitting diode (LED). Molecular LEDs are under intense investigation,[2] but to our knowledge there is only one unspecific report from the patent literature[3] that describes this type of LED sensor.

Because it is a better film former than **1**, we chose to study tetrakis(*p*-decylphenylisocyano)platinum tetranitroplatinate (**2**) as the stacked platinum complex. This material[4] is also vapochromic as described above, except that the color change does not reverse when the vapor is removed. The color can, however, be changed by introducing another vapor,[4] and switched back and forth in a reversible manner with the sequential use of two different vapors. In the present study the quantum yield for photoluminescence (PL) from a thin film of **2** was 3.8% (excited at 438 nm, measured at 540 nm). Devices were prepared by spin casting **2** from toluene onto ITO coated glass, followed by vapor deposition of aluminum. This gave single layer devices which were very resistive, unstable, and did not show rectification. No electroluminescence (EL) was observed before electrical breakdown.

Recently, we have shown that it is possible to form single layer LEDs, ITO/**4**/Al, by anodically oligomerizing compound **3**, tris(*p*-thienylphenyl)amine, to form **4**.[5] Because the layer of **4** is insoluble in solvents such as toluene it seemed possible to spin cast a second layer of **2** on top of **4** without layer interdiffusion. In this way **4** could be used as a hole transport layer to make a two-layer device. This approach succeeded when we prepared ITO/**4**/Alq$_3$/Al using the well-known emitter, aluminum tris(8-hydroxyquinoline).[6] Here, we prepared the two-layer device ITO/**4**/**2**/Al by electrooligomerizing **3** (700 nm layer of **4**) onto ITO, spin coating **2** from toluene (200 nm layer of **2**), and vapor depositing aluminum (200 nm). As previously described[5] the electrooligomerization was performed by oxidizing **3** in acetonitrile, lithium perchlorate providing the oxidized form of **4**, and then reducing it to form the neutral **4**. The amount of **4** on the surface was estimated coulometrically and spectroscopically.

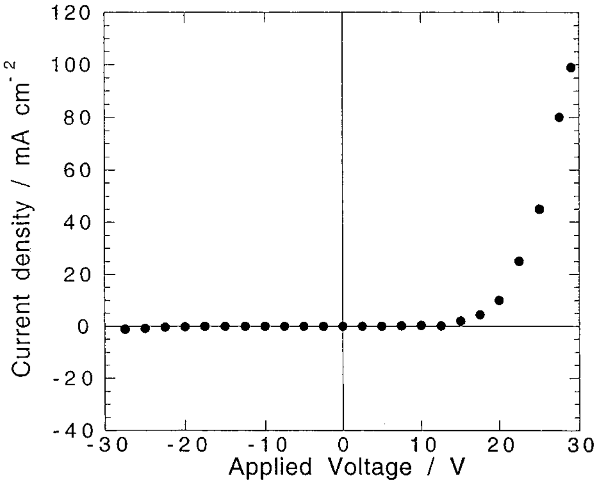

Figure 1. *j*−V characteristics of ITO/**4**/**2**/Al. Voltage refers to the ITO electrode.

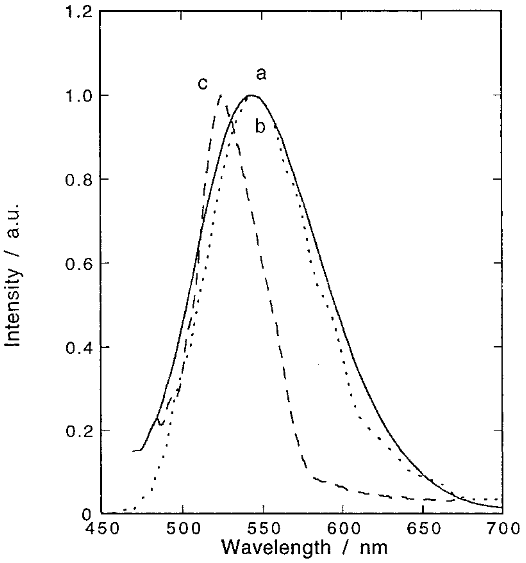

Figure 2. Spectra of **2** (PL (a) and, EL (b)) and **4** (PL (c)).

The device ITO/**4**/**2**/Al (2 mm diam) gave rectification of the applied current (Figure 1) favoring electron flow from Al through the molecular layers to ITO. The EL spectrum corresponded closely to the PL spectrum of **2** cast from toluene onto ITO (λ_{max} 540 nm, Figure 2). The current/EL intensity curve was nearly linear up to 25 V, and we estimate that the photon/electron efficiency is about 0.01%. When the device was exposed to argon saturated with acetone vapor, the EL spectrum changed dramatically to λ_{max} 575 (Figure 3). This spectrum is quite different from the PL spectrum of **4**. Thus, it appears that the EL comes primarily from **2**, not **4** which emits at lower wavelength. If the

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[1] Exstrom, C. L.; Sowa, J. R.; Daws, C. A.; Janzen, D. E.; Mann, K. R. *Chem. Mater.* **1995**, *7*, 15. Daws, C. A.; Exstrom, C. L.; Sowa, J. R.; Mann, K. R. *Chem. Mater.* **1997**, *9*, 363.

[2] Friend, R. H. In *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundstrom, I., Ranby, B., Eds.; Oxford University Press: Oxford, 1993; Chapter 21. Heeger, A. J. In *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundstrom, I., Ranby, B., Eds.; Oxford University Press: Oxford, 1993; Chapter 4. Friend, R. H.; Greenham, N. C. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: New York, 1996. Yang, Y. *MRS Bull.* **1997**, June, 31. Tsutsui, T. *MRS Bull.* **1997**, June, 39. Salaneck, W. R.; Bredas, J. L. *MRS Bull.* **1997**, June, 46.

[3] Aldey, D. E.; Harvey, T. B. U.S. Patent 5,629,533, 1997.

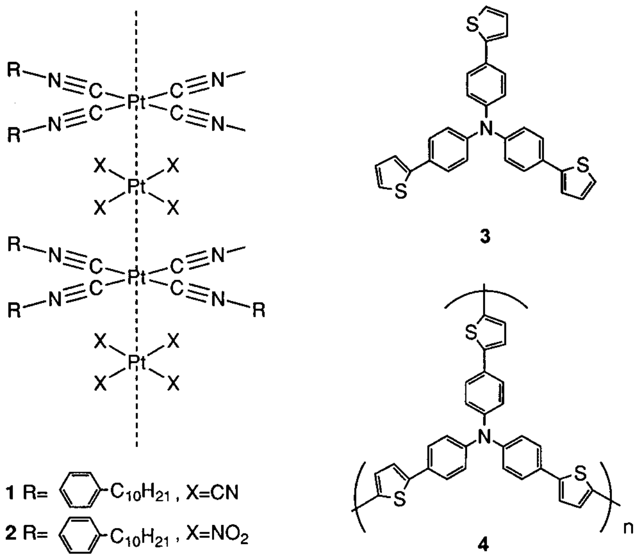
[4] Exstrom, C. L. Ph.D. Dissertation, University of Minnesota, 1995. **2** was prepared from a mixture of *p*-decylphenyl isocyanide, *cis*-(CH$_3$CN)$_2$PtCl$_2$, and [(*n*-C$_4$H$_9$)$_4$N][Pt(NO$_2$)$_4$ in acetonitrile. The purified product gave appropriate combustion analysis and spectroscopic data.

[5] Kunugi, Y.; Tabakovic, I.; Canavesi, A.; Miller, L. L. *Synth. Met.* **1997**, *89*, 227.

[6] Unpublished work of Baruch Zinger, University of Minnesota, 1997.

S0002-7863(97)03627-5 CCC: $15.00 © 1998 American Chemical Society
Published on Web 01/07/1998

Chart 1



device is left at zero current for several days, open to the room atmosphere, no change in the spectrum is seen. Exposure of the device to toluene vapor in argon causes the spectrum to revert to the original.

Molecular LEDs are often not very stable when they are in use, especially in air. Use as a sensor, however, only requires that the device be occasionally pulsed. Using a 1 mA cm^{-2}, 3 s pulse every 5 min gives a stable emission intensity for an hour. When acetone vapor in argon was introduced the spectrum did not change for about 5 min, but then quickly shifted to the longer wavelength (Figure 4). Since there is no evidence that the color changes from the outside diameter of the device moving inward, and because the rate of change is independent of the diameter of the device, we hypothesize that the acetone penetrates through the thin (pinholed?) aluminum film. This is consistent with the sudden change of the color after a few minutes (as the acetone diffusion front reaches the molecular layers and rapidly diffuses into them, changing the structure and EL spectrum).

These preliminary results suggest that it will be possible to have a device of this type report on the arrival of certain vapors with a pulse of light. Since different organic vapors elicit different optical responses, a variety of chemicals can be detected. Using reversible examples of stacked complexes may provide the possibility of quantifying the response, and using alternative device geometries should improve the response time.

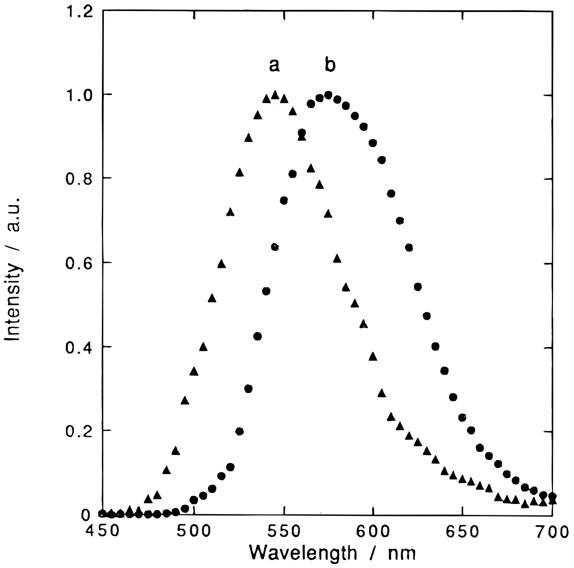


Figure 3. EL spectra of ITO/**4**/**2**/Al (a) before and (b) after exposure to acetone vapor.

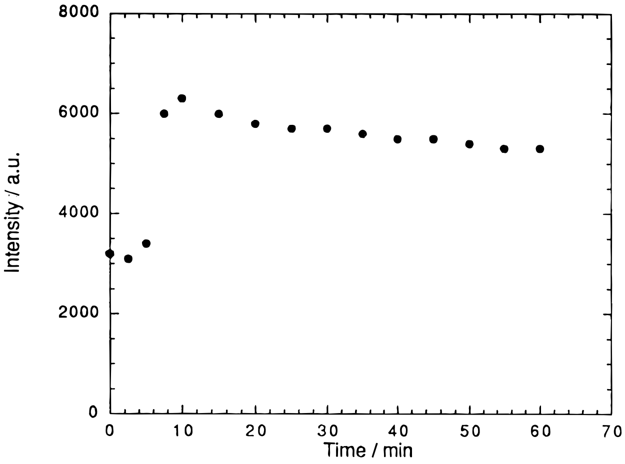


Figure 4. Time dependence of the EL at 600 nm after exposure to acetone vapor at time zero.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged. The samples of compounds **2** and **3** were prepared by Carolyn Anderson and Andrew Schmidt, respectively.

JA973627Z