

A Novel Optical Transistor Device based on Photo-induced Proton transfer Reactions

Yang Hwang Zen, and Chong Mou Wang*

National Taiwan Normal University, Department of Chemistry, Taipei 11718, Taiwan, ROC

An optical transistor device is fabricated with thin-film lumichrome (7,8-dimethylalloxazine) on conductive SnO₂ glass; the cathodic current recorded with the emitter electrode is substantially enhanced when the electrode is illuminated (365 nm).

Numerous studies have reported photo-induced proton transfer reactions.¹⁻¹⁰ However, reports of optical rectification are relatively rare. We now describe an optical transistor device based on photo-induced proton transfer with lumichrome, 7,8-dimethylalloxazine.¹¹

Typical emission spectra (Fig. 1) of lumichrome show two emission bands at 470 and 530 nm. Variation of the solution pH results in little change of the 530 nm band, whereas the emission at 470 nm shifts to a shorter wavelength 450 nm in KOH solution (pH 12). Since the associated acidity constants with the N-1 and N-10 positions are *ca.* 10⁻² and 10⁻⁵, respectively, the 530 nm band is tentatively assigned to the emission from the excited tautomer flavin during phototautomerization,¹¹ and the emissions at 470 and 450 nm probably result from the excited protonated and deprotonated transient states **A** and **B** in Scheme (1), respectively.

Based on the Forster cycle,¹² the p*K_a* difference (*i.e.* p*K_a** - p*K_a*) associated with N-10, between light and dark, is evaluated as *ca.* 1.9, suggesting that the photo-excited N-10 is expected to be a stronger base than its ground state.

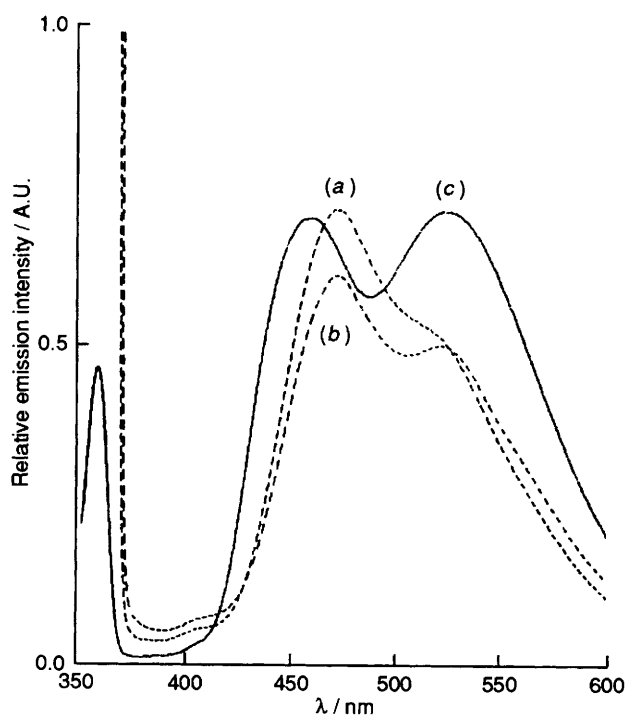
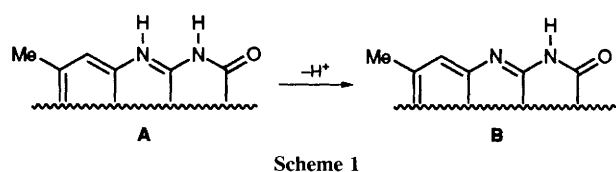


Fig. 1 Fluorescence spectra recorded with lumichrome (*ca.* 10⁻⁸ mol dm⁻³) in various pH solutions: (a) perchloric acid (pH 2); (b) phosphoric acid (pH 4); (c) KOH (pH 12); λ_{ex} = 365 nm

CV [Fig. 2(a)] recorded with the thin-film lumichrome electrode (Fig. 3),† illustrate a weak quasi-irreversible cathodic peak at -0.6 V vs. SCE, showing a characteristic wave from a pyridine-containing free base. When the electrode is illuminated, a current enhancement is recorded.

According to the photoelectrochemical behaviour observed in Fig. 2(a), a photo-induced proton transfer reaction occurring at the N-10 position is strongly indicated, supported by the control experiments that current enhancement can be

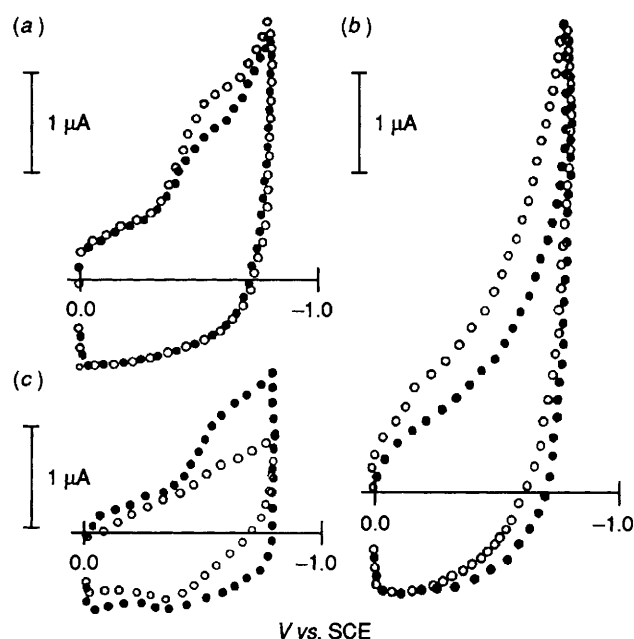


Fig. 2 CV recorded in MeCN-H₂O (10:1) solutions containing lumichrome (1 mmol dm⁻³) and LiClO₄ (0.1 mol dm⁻³) under illumination (○) or in the dark (●): (a) lumichrome only, (b) with acetic acid (5%) and (c) with pyridine (10%); scan rate 50 mV s⁻¹

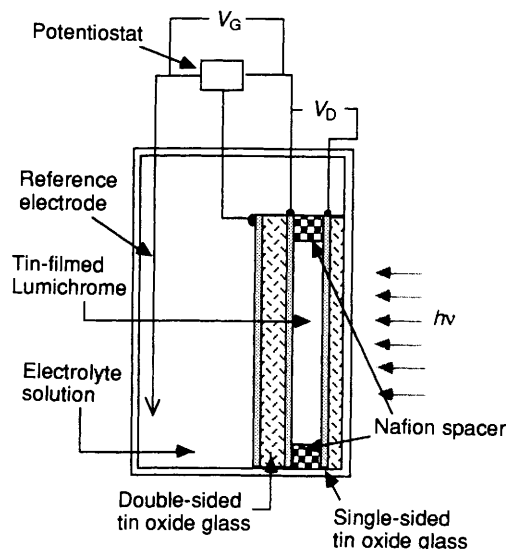


Fig. 3 Representation of the optical transistor device

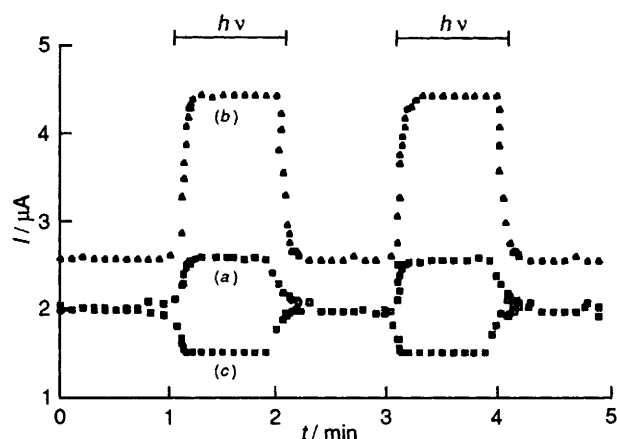


Fig. 4 Chronopotentiograms recorded under the same conditions as the CV, $E_{\text{appl}} = -0.6 \text{ V vs. SCE}$

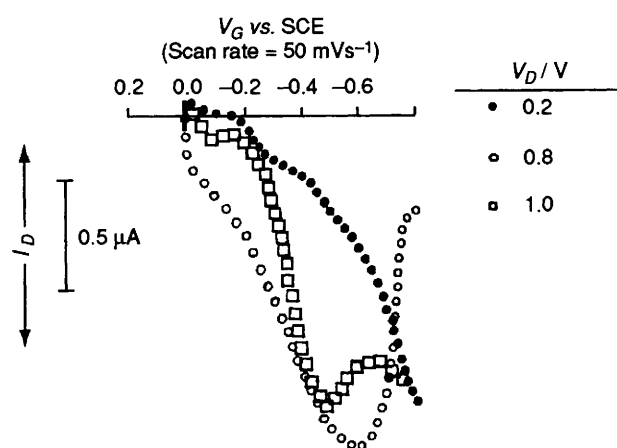


Fig. 5 Dependence of drain current on the gate and drain potentials

achieved with the incorporation of proton donor, like HCl, without light, which is consistent with ΔpK_a (Fig. 1).

A greater amplification of photo-response is observed [Fig. 2(b)] when a proton-transfer catalyst, acetic acid, is incorporated, in contrast with the observations in Fig. 2(c) that current reversal is detected when pyridine, a competing proton acceptor (ΔpK_a ca. 3), is introduced. The chronopotentiograms (Fig. 4) indicate the photosignal is intensified by a factor of ca. 5 with 5% acetic acid, and the polarity of the

photo-response can be reversely tuned when pyridine (10%) is incorporated. The drain current output from the device is gate-potential dependent (Fig. 5); the drain current is optimized at $V_G = -0.6 \text{ V vs. SCE}$, when V_D is held at $+0.8 \text{ V vs. the emitter}$. Under such a condition, the drain current collection efficiency, I_D/I_E , is estimated to be 20%.

We thank the National Science Council, Republic of China, for financial support (Grant No. NSC 84-2113-M-003-010).

Received, 22nd August 1994; Com. 4/05116E

Footnote

† The emitter was constructed by dip-coating with $10 \mu\text{l cm}^{-2}$ of lumichrome (1 mmol dm^{-3} in MeCN) on one face of a double-sided tin oxide-quartz plate (ca. 1 cm^2) which was spaced by $10 \mu\text{l cm}^{-2}$ of Nafion (2 mm wide; 2.5 mass % in alcohol, Aldrich) around the periphery of the electrode; the other part of the tin oxide slide served as the counter electrode. The spacer thickness was estimated to be ca. $2 \mu\text{m}$.¹³ After drying in air, the emitter was combined face-to-face with another piece of bare tin oxide (drain). The whole device was then sited in a quartz cell filled with electrolyte. In the case with acetic acid or pyridine, the proton catalyst was incorporated with the electrolyte directly. Before each measurement, the device was allowed to soak for 1 min. Illumination was by a 500 W mercury lamp with a 365 nm filter; the flux was ca. 14 mW cm^{-2} .

References

- 1 A. Weller, *Z. Electrochem.*, 1956, **60**, 1144.
- 2 S. Nagoaka, N. Hirota, M. Sumitani and K. Yoshihara, *J. Am. Chem. Soc.*, 1983, **105**, 4220.
- 3 S. Nagoaka, M. Fujita, T. Takemura and H. Baba, *Chem. Phys. Lett.*, 1986, **123**, 489.
- 4 S. Nagoaka and U. Nagashima, *Chem. Phys.*, 1989, **136**, 153.
- 5 S. Nagoaka, U. Nagashima, N. Ohta, M. Ujita and T. Takemura, *J. Phys. Chem.*, 1988, **92**, 166.
- 6 A. Costela, J. M. Munoz, A. Douhal, J. M. Figuera and A. U. Acuna, *Appl. Phys.*, 1989, **B49**, 545.
- 7 M. Blank, L. M. Soo, N. H. Wassermann and B. F. Erlanger, *Science*, 1981, **214**, 70.
- 8 J. D. Winker and K. Deshayes, *J. Am. Chem. Soc.*, 1987, **109**, 2190.
- 9 S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manake, *J. Am. Chem. Soc.*, 1981, **103**, 111.
- 10 P. Haberfield, *J. Am. Chem. Soc.*, 1987, **109**, 6178.
- 11 J. D. Choi, R. D. Fugate and P.-S. Song, *J. Am. Chem. Soc.*, 1980, **102**, 5293.
- 12 B. Marciniak, H. Kozubek, and S. Paszyc, *J. Chem. Educ.*, 1992, **69**, 247.
- 13 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, 1980, **102**, 6641.