

Electroluminescence from the Evaporated Thin Film of Excited-state Intramolecular Proton Transfer Dye

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Organic electroluminescent devices (OLEDs) have been intensively investigated in the last decade with the aim of application for full-color flat panel displays.^{1,2} It has been demonstrated that a variety of organic materials such as fluorescence dyes, organometallic complexes, and fully conjugated polymers can be used as hole or electron transport layers (HTL or ETL), and emission layer (EML) in the form of vacuum-deposited or spin coated thin film.^{3,4} So far, there have been a great number of studies for new EML materials to achieve higher efficiency and full color emission. Very recently we reported a new type of electroluminescence based on the excited-state intramolecular proton transfer (ESIPT) with a photo-tautomerizable semi-rigid polyquinoline (PQH, Figure 1a).⁵ ESIPT is an excited-state tautomerization from enol form to keto form occurring in the intramolecularly hydrogen-bonded molecules. As schemed in

Figure 1b, the different absorbing (enol) and emitting (keto) species give rise to an abnormally large Stokes shift without self-reabsorption. Therefore this four-level photophysical process facilitates stimulated emission with high optical net gain.⁶

Herein are reported the ESIPT-electroluminescence from vacuum-deposited thin film of a photo-tautomerizable quinoline dye (MQ).

Experimental Section

MQ was prepared by Friedländer reaction between bis-(aminoketone) (**1**) and 2-hydroxy-4-methoxyacetophenone (**2**, Aldrich Chemical Co.) in the presence of *m*-cresol and P₂O₅ according to the reported method (Scheme 1).^{7,8} The final product was purified by column chromatography eluting with ethyl acetate and *n*-hexane (volume ratio increasing from 1 : 2 to 1 : 1) with the yield of 30%.

MQ: ¹H NMR (CDCl₃, ppm): 3.84 (s, 6H), 3.87 (s, 6H), 6.51 (dd, *J* = 8.79, 2.66 Hz, 2H), 6.60 (d, *J* = 2.66 Hz, 2H), 7.00 (d, *J* = 8.79 Hz, 4H), 7.40–7.50 (m, 8H), 7.82 (s, 2H), 7.84 (d, *J* = 8.79 Hz, 2H), 8.02 (d, *J* = 9.15 Hz, 2H). *m/z* (EI) calcd for C₄₆H₃₆N₂O₇, 728.79, found 728.

Absorption spectra were recorded on a HP 8452A diode array spectrophotometer. Emission spectra were obtained on a fluorescence spectrophotometer (Shimadzu, RF-5301PC). For film state optical measurement, MQ was vacuum-deposited onto a quartz substrate as described below.

For the fabrication of OLED, indium-tin oxide (ITO) coated glass with a sheet resistance of 20 Ωcm⁻² was patterned by the vapor of a mixed solution of HNO₃ and HCl in a volume ratio of 3 : 1. The patterned ITO-coated glass slides were cleaned by sequential ultrasonication in acetone, methanol and 2-propanol for 20 minutes, then dried in a stream of nitrogen. The conducting polymer solution of poly(3,4-ethylenedioxy-2,5-thiophene) doped with polystyrene sulphonate (PEDOT : PSS) (Bayer) was spin coated under 3300 rpm for 1 min and dried at 150 °C for 30 minutes. The electrical conductivity of this film measured by the four-line probe method was 10 S cm⁻¹. Thin film deposition was carried out by a ULVAC VPC-260 (Japan) evaporation apparatus. MQ was thermally evaporated from a tungsten boat at a deposi-

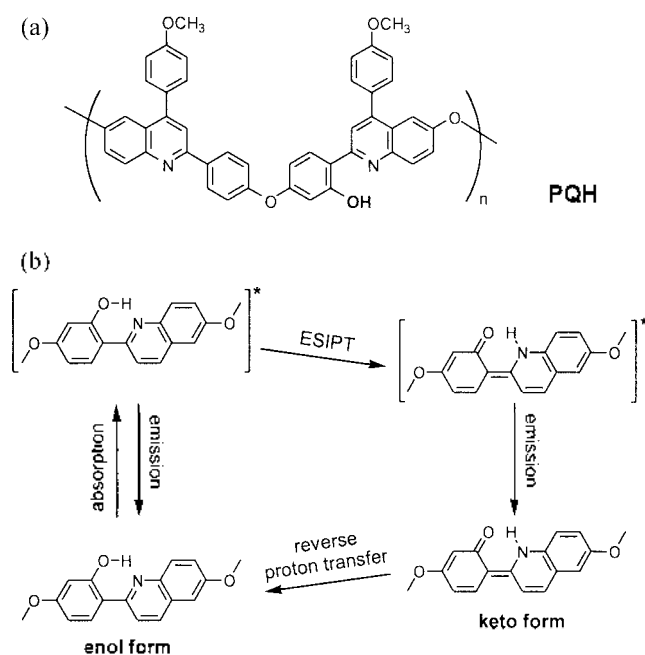
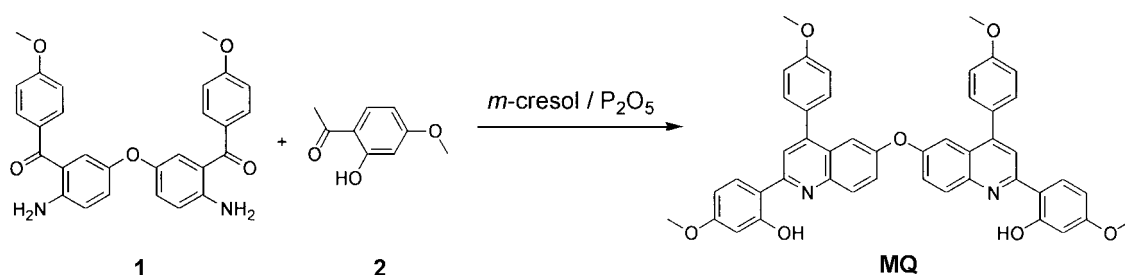


Figure 1. (a) Semi-rigid polyquinoline (PQH) exhibiting ESIPT. (b) Photochemical processes of photo-tautomerizable compound.

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Scheme 1. Synthesis of photo-tautomerizable low molecular weight quinoline (MQ).

tion rate of 2–3 Å/s with a base pressure of 5×10^{-6} Torr, as measured by quartz crystal thickness monitor placed near the substrate. The thickness of MQ layer was *ca.* 600 Å. The Li:Al alloy (Li 0.2 wt %) electrode (1500 Å thick) was vapor deposited using the same apparatus. The active area of the device was 4.9 mm².

The current and luminescence intensity as a function of applied field were measured using an assembly consisting of a PC-based DC power supply (HP 6623A) and a digital multimeter (HP 34401). A light power meter (Newport Instruments, Model 818-UV) was used to measure the device light output in microwatts.

Results and Discussion

The purified MQ is a yellow crystalline powder with a melting point at 98 °C and forms an extremely clear film by vacuum deposition. Figure 2 shows optical properties of MQ in chloroform solution ($\sim 10^{-5}$ M) and also those of vacuum-deposited film. Absorption of MQ solution comprises three main bands. According to the semiempirical quantum chemical calculation in our previous work, the conjugation between quinoline and pendant phenyl ring attached at its 4-position is broken owing to a large torsional angle of *ca.* 67°. Moreover the excitation spectrum, though not shown here, indicated that only the two bands above 300 nm are attributed to the transition of π -conjugated unit or 2-quinolin-2-yl-phenol moiety. Vacuum-deposited MQ film showed almost the same absorption feature (band structure, peak position) with that of solution, indicating the absence of remarkable intermolecular electronic interaction such as aggregation. It is noted that the kink structure of MQ by central ether linkage along with the distorted pendant phenyl rings would prevent the intermolecular association of π -conjugated unit and also the recrystallization in the amorphous film state. Small bathochromic shift (~ 6 nm) of the longer wavelength band is ascribable to the slightly extended conjugation length by enhanced planarity since the intermolecular proximity in the film state would prefer more planar conformation of π -conjugated unit.

In contrast to the virtually identical absorption spectra, photoluminescence of MQ showed significant differences in intensity and spectral feature in the solution and film states. When excited at 370 nm, MQ film gave orange emission while MQ solution showed no detectable emission. One possible explanation for this fluorescence quenching in

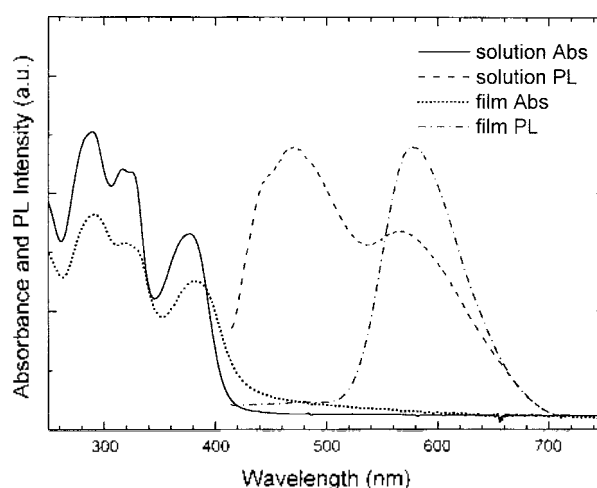


Figure 2. Absorption (Abs) and photoluminescence (PL) spectra of MQ solution (10^{-5} M in chloroform) and vacuum-deposited film. Weak PL of solution was measured with high sensitivity and the magnified spectrum was drawn in this figure.

solution can be given in the sense of twisted intramolecular charge transfer (TICT) state connected with a large amplitude torsional vibration between quinoline and hydroxy-phenyl groups.⁹ The magnified spectrum of solution emission measured with high sensitivity consists of dual bands similar to PQH solution emission: the shorter wavelength band at 470 nm is attributed to the enol form and the longer wavelength one at 570 nm to the keto form.⁵ As shown in Figure 2, MQ film gave only a large Stokes shifted keto emission peaking at *ca.* 580 nm. The absence of enol emission means that the excited enol form decays mainly to the excited keto form rather than radiatively to the ground enol form by effective ESIPT. It is probably because the torsional motion is virtually frozen in the film state so that the intramolecular hydrogen bond is more favored energetically.

Electroluminescence property of MQ was investigated using a two-layer device configuration. Since the quinoline is a π -electron deficient system which can potentially contribute toward electron injection/transport and hole blocking properties,³ MQ film is expected to act as ETL as well as EML. Poly(3,4-ethylenedioxy-2,5-thiophene) doped with polystyrene sulphonate (PEDOT:PSS) was chosen as non-emissive HTL and inserted between ITO and MQ layer. This two-layer device exhibited typical electroluminescence characteristics as shown in Figure 3. Electroluminescence spectrum

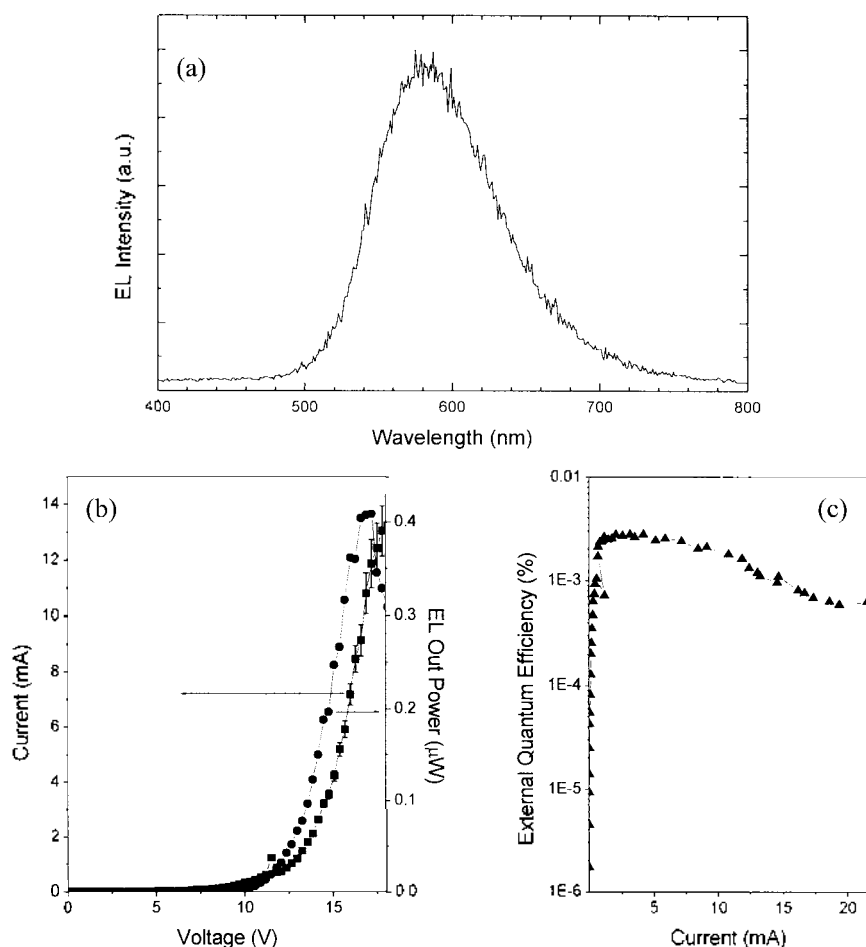


Figure 3. Electroluminescent (EL) properties of ITO/PEDOT:PSS/MQ/Al:Li device: (a) EL spectrum, (b) current-voltage-luminance (I - V - L) characteristics, and (c) external quantum efficiency.

in Figure 3a is exactly the same with photoluminescence spectrum of MQ film, giving only keto emission. The current-voltage-luminance (I - V - L) characteristics and the external quantum efficiency are shown in Figure 3b and 3c, respectively. It is observed that the charge injection is initialized at *ca.* 7 V while the emission is turned on at *ca.* 8 V. This voltage difference is mainly due to the unbalanced injection and transport of hole and electron. The external quantum efficiency showed the maximum value of 0.0028% at current density of 430 A/m². The electroluminescent keto emission can be understood as electrically generated ESIPT: the exciton is produced in the predominantly existing enol form by the recombination of hole and electron within MQ layer and then this enol exciton mainly decays to the excited keto form by effective proton transfer in the film state, followed by the radiative relaxation of the excited keto form.

In summary, we demonstrated OELD with a novel vacuum-deposited EML material (MQ) based on the electrically generated ESIPT. Its large Stokes shift without self-reabsorption would be promising for the electrically pumped organic laser diode requiring high optical net gain.

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