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Properties of a new pyrazoline derivative and its application in electroluminescence

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As evaporated thin film and in solution, the absorption spectra, photoluminescence, electrochemistry and electroluminescence of the newly synthesized 1,3-diphenyl-5-pyren-2-yl-4,5-dihydro-1*H*-pyrazole (DPP) were investigated. The absorption spectra cover the whole near-ultraviolet region. At lower concentrations, the fluorescence emission is at 415 nm; at higher concentrations, a new face to face excimer emission appears on longer wavelengths; in the thin film state, the fluorescence emission becomes a single band peaking at 470 nm. Cyclic voltammetry of DPP and the hole transport material as evaporated thin films on ITO (indium tin oxide) was compared with that in solution and was used to determine the energy levels. The electric field strength dependent electroluminescent behavior of DPP was explained according to the energy levels by a tunneling mechanism, ruling out the possible cause by an excimer or exciplex formation. At a drive voltage of 18 V, the blue electroluminescence reached 2400 cd m^{-2}.

Introduction

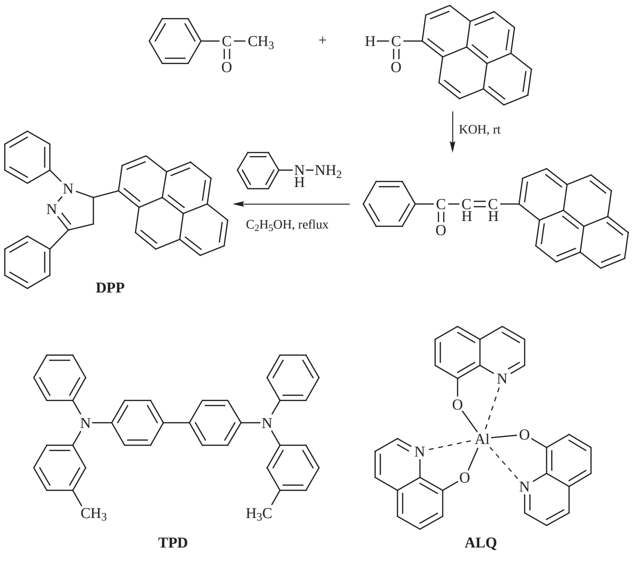
The past decade has seen extensive interest in electroluminescence (EL) from organic light-emitting devices, in view of possible application in low-cost, full-color flat-panel displays.[1–3] Usually, devices comprise charge injecting electrodes sandwiching thin film organic hole or electron transport layers and a light-emitting layer. Under high electric field strength ($\sim 10^8$ V m^{-1}), holes from the anode and electrons from the cathode enter the occupied states of a hole transport layer and the unoccupied states of an electron transport layer respectively. They will then form negatively and positively charged polarons in the organic layers. These polarons migrate under the influence of the applied electric field, forming a polaron exciton with an oppositely charged species and subsequently undergoing radiative recombination.[4,5]

Testing new materials is of great importance for understanding device physics and improving device performance. Pyrazolines are known hole transport materials.[6,7] Sano *et al.* have reported pyrazoline dimers as the hole transport materials in organic EL devices.[8] In this article, a derivative of pyrazoline, DPP (1,3-diphenyl-5-pyren-2-yl-4,5-dihydro-1*H*-pyrazole), was synthesized and used as the light-emitting layer of the triple layered EL device based on its strong blue-colored fluorescence and its aligned ionization potential with the hole transport layer. For a thorough understanding of its properties, its absorption, photoluminescence (PL) and electrochemistry in solution and as an evaporated thin film were compared. A revised cyclic voltammetric (CV) method, with evaporated organic thin film on ITO as the working electrode, was used for the determination of energy levels. Based on the energy levels, the electric field strength-dependent electroluminescence behavior was explained.

Experimental

Materials

N,N′-Bis(3-methylphenyl)-*N,N′*-diphenylbenzidine (TPD) was purchased from Aldrich. Aluminium tri(quinolin-8-olate) (ALQ) was synthesised by the reaction of $AlCl_3$ with 8-hydroxyquinoline in alcohol and was recrystallized from $CHCl_3$ then purified by vacuum sublimation. The procedure for the synthesis of DPP is as follows: (i) synthesis of DPP precursor: 0.6 g (5 mmol) acetophenone and 1.15 g (5 mmol) pyrenecarbaldehyde in 6 ml ethanol were mixed with a solution of 0.36 g (6.4 mmol) potassium hydroxide in 3 ml water. The reaction mixture was stirred for 24 h at room temperature. The crystalline precipitate was filtered, washed with ethanol and recrystallized from ethanol to give 1 g (60%) yellow crystals (DPP precursor); (ii) 1 g (3 mmol) DPP precursor and 0.7 g (6.5 mmol) of phenylhydrazine in 5 ml ethanol were refluxed for 6 h. The product was filtered and washed with ethanol to give 1.1 g yellow solid product (crude DPP). It was then purified by silica gel chromatography (eluent chloroform–petroleum ether (1:4)) and recrystallized from THF to give the colorless DPP crystals, mp 254–256 °C. ^{1}H NMR ($CDCl_3$): 6.75–8.45 (19H), 6.25–6.43 (1H), 4.17–4.28 (1H), 3.25–3.35 (1H); MS: DPP^+, 422; Anal., calc. (found) for $C_{31}H_{22}N_2$: C 88.15 (87.76), H 5.21 (5.37), N 6.64 (6.64). The synthesis procedure is shown in Scheme 1.



Scheme 1 Synthetic route of DPP and molecular structure of TPD and ALQ.

Preparation of the EL device and the electrode

Preparation of the EL devices: The substrate is an indium–tin oxide (ITO) coated glass with a sheet resistance of 30 $\Omega\square^{-1}$. With one-third of the ITO coating stripped off by hydrochloric acid, the substrate was cleaned by ultrasonication first in a detergent solution then in a mixture of isopropyl alcohol and water (1 : 1) followed by toluene degreasing. After drying under an infrared lamp, the substrates were immediately loaded into the vacuum chamber. The organics were then successively thermally evaporated onto the ITO from molybdenum crucibles with rates in the range of 0.1–0.3 nm s^{-1} below a pressure of 1×10^{-5} Torr. The aluminum cathode was evaporated from a tungsten wire basket at higher rates (0.8–1.2 nm s^{-1}) in a single vacuum run.

The single layer and double layer working electrodes for cyclic voltammetric measurements were prepared by thermally evaporating the tested materials onto ITO by the same procedure as that for preparing the EL device.

Instrumentation

The absorption measurements were obtained using a Shimadzu UV-3100 spectrophotometer. The photoluminescence and electroluminescence were measured with a Hitachi model 850 fluorescence spectrophotometer. The brightness of the EL device was measured with a ST-86LA spot photometer and a closeup lens providing a focal spot of 5 mm. The layer thicknesses were controlled *in vacuo* by an IL-1000 quartz crystal monitor, and were also measured with a Dektak[3] surface profile measuring system. Cyclic voltammetric experiments were performed using a CH Instruments Voltammetric Analyzer model 600. For solution CV, the working, auxiliary and reference electrodes were a 0.5 cm^2 glassy carbon disk, a Pt wire and a Ag/AgCl wire, respectively; 0.1 M Bu_4NClO_4 in *N*,*N*-dimethylformamide (DMF) was the supporting electrolyte. Film CVs were recorded by using the evaporated thin films on ITO substrate as the working electrode, saturated calomel (SCE) as the reference and a Pt wire as the auxiliary electrode in 0.1 M KCl aqueous solution.

Results and discussion

Absorption spectra

Fig. 1 shows the absorption spectra of DPP in solution and in the thin film state. The absorption is a result of the combination of two chromophores (the pyrene and pyrazoline groups) and covers the entire 200–400 nm region. As Fig. 1 shows, in solution, the absorption bands are sharp lines. As evaporated thin films on quartz substrate, the absorption bands become ‘flat’ and shift toward the longer wavelength region. This is because the intermolecular distances in the film state are reduced and the repulsion of the occupied π orbitals raises the energy level of the ground state.

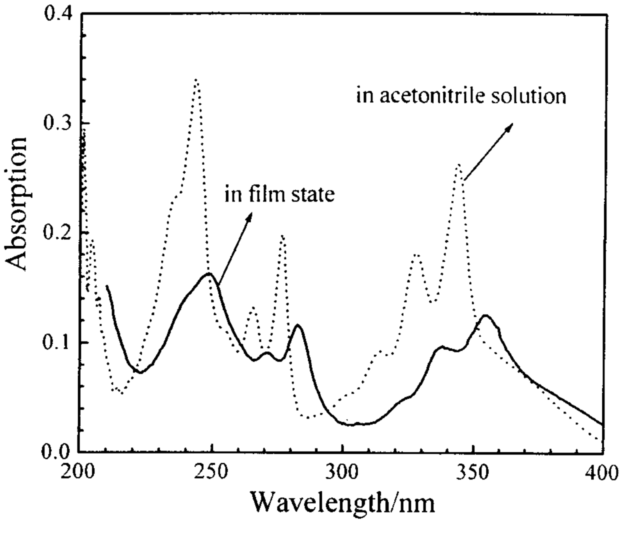


Fig. 1 Absorption spectra of DPP in *ca.* 1×10^{-4} M acetonitrile solution and in the thin film state which was measured by evaporating DPP on a quartz substrate.

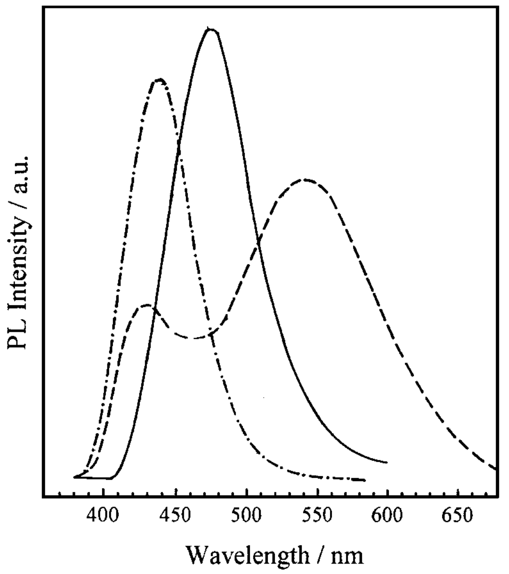


Fig. 2 Photoluminescence spectra of DPP, –·–·–, 1×10^{-6} M acetonitrile solution; – – –, 1×10^{-4} M acetonitrile solution; —, thin film state. All were excited at 350 nm.

Photoluminescence

A similar effect of intermolecular interaction is found in the PL spectra. As Fig. 2 shows, at a concentration of 1×10^{-6} M, the fluorescence spectrum is composed of pure DPP monomer emission. As the concentration of DPP increases, the monomer emission decreases in intensity and a new fluorescent emission appears on the longer wavelength side of the monomer emission and increases in intensity. This new emission is due to the pyrene excimer,[9] a result of strong π electron repulsion as the separation distance is reduced for the two DPP molecules at higher concentration. However, when the intermolecular distance is further reduced as in the thin film state, the fluorescence emission becomes a single band peaking at 470 nm. The ‘red shift’ of the fluorescence emission is due to the ground state energy increase by the increased intermolecular interaction as a result of closer packing of the molecules in the film state. The reason for the disappearance of the excimer emission is that in the film state, the pyrenyl substituents cannot easily align face to face to favor the maximal overlap of the π orbitals.

Electrochemistry

Fig. 3(a) shows the CV of DPP in DMF solution and as a single layer film on ITO substrate. In solution, DPP reveals two oxidation peaks at 0.75 V and 1.24 V. The ill-defined reduction peak indicates the reduction process is incomplete. The two oxidation processes may originate from the electron loss of the two nitrogen atoms. However, in the thin film state, only one oxidation process occurs and the oxidation peak is broader than that in solution. This comparison shows molecules in the thin film state are less electroactive than in solution. Several possible factors related to the solid state nature of the film may complicate the interpretation of this reduced electroactivity. For example, electron transfer through molecules in the film state is less effective than in solution; a

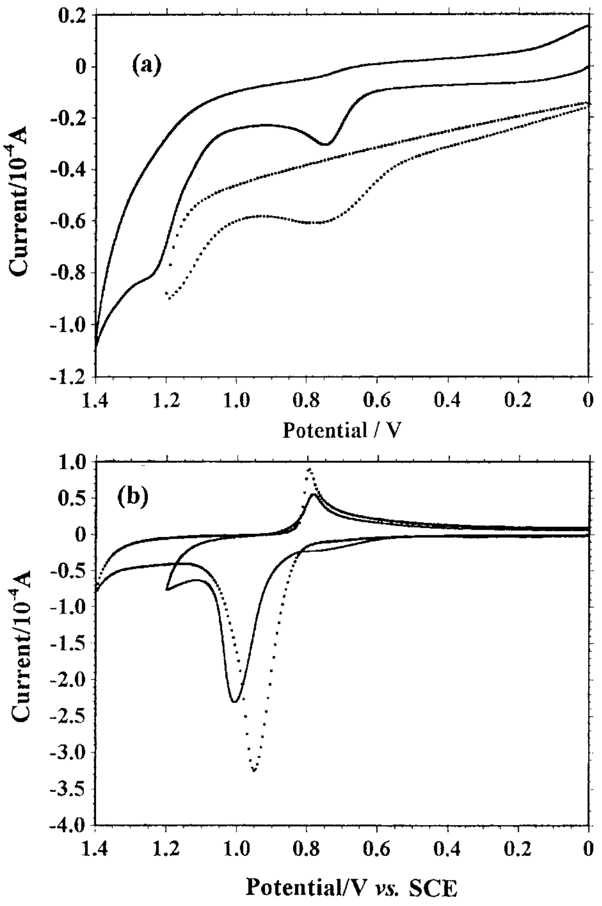


Fig. 3 (a), CV of DPP, —, in DMF solution, ..., ITO/DPP single layer film. (b), CV of —, ITO/TPD/DPP electrode, ..., ITO/TPD single layer.

solid/solid interface between ITO and organic materials introduces an additional barrier prohibiting the transport of electrons.

Fig. 3(b) shows the CV of the double layered ITO/TPD/DPP electrode as compared with a single layer TPD on ITO. For the ITO/TPD/DPP electrode, the broad wave at *ca.* 0.75 V originated in the oxidation process of DPP, identical in peak position to but smaller in peak intensity than that of the single layered electrode; the sharp negative current peak at *ca.* 1.0 V and the positive current peak at *ca.* 0.78 V correspond to the oxidation of TPD neutral molecule and the reduction of TPD$^+$ cation. The oxidation of TPD buried by one layer of DPP (1.0 V) needs a higher potential than single layer TPD (0.95 V).

Ionization potential (IP) is defined as the minimum energy necessary to bring an electron from the material into vacuum. It is the difference between orbital energy at infinite distances and the energy of the highest occupied orbital. Use of solution electrochemical processes to describe electron-transfer reactions in the film state is predicted upon the assumption that differences in ionization potentials of these molecules in solution are equal to or smaller than those same energy differences in the film state. For electroluminescent or other optoelectronic applications, devices are usually prepared by vacuum depositing the materials onto ITO. In cyclic voltammetric measurements, using ITO with pre-evaporated thin films on it as working electrodes, the driving force for the oxidation of TPD and DPP would be more like that in an electroluminescent device, because electron gain and loss occurs in the thin film state. From the CV of TPD and DPP as precast films on ITO, the IPs for DPP and TPD are 5.50 eV and 5.61 eV (the medium of the redox peaks for the single layer TPD) respectively. These values are higher than those obtained from

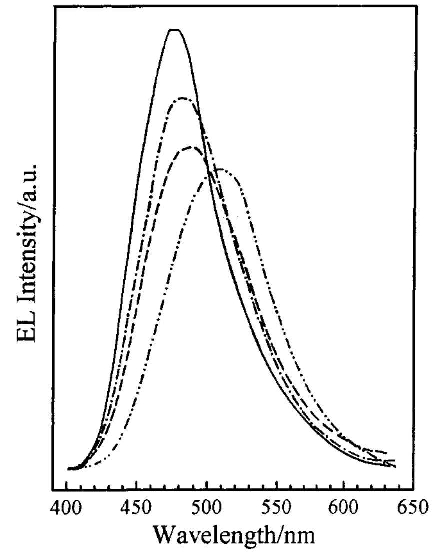


Fig. 4 Electroluminescence spectra of the ITO/TPD/DPP/ALQ/Al device (each layer is 35 nm) under different drive voltages, 8 V (– – –), 12 V (–·–·–) and 16 V (—). When the ALQ layer is increased to 50 nm, the emission stays at 520 nm (–··–) under drive voltages 8–16 V.

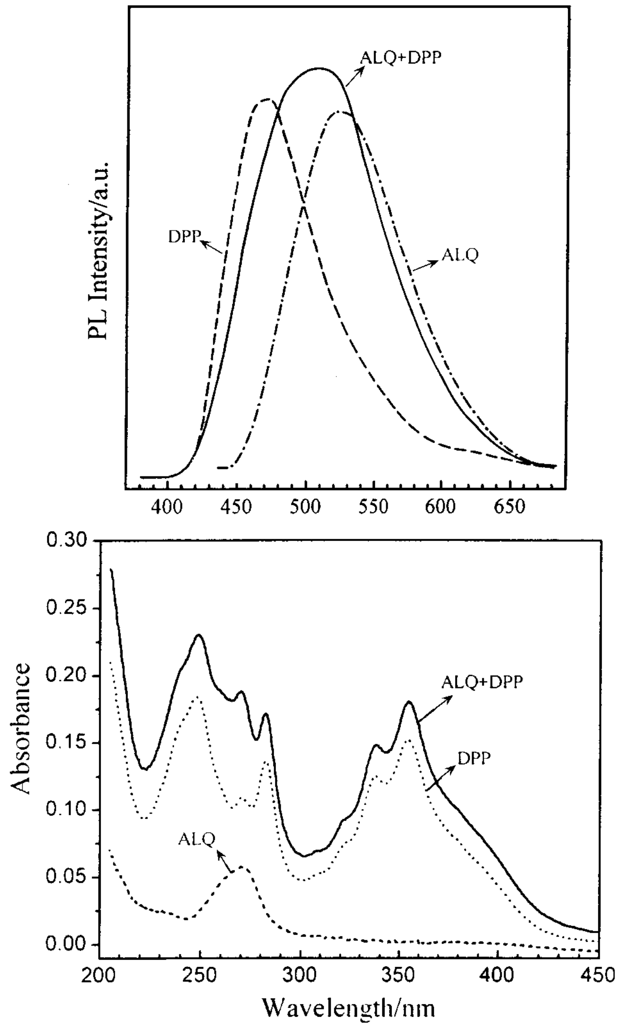


Fig. 5 Photoluminescence and absorption spectra of single layer film quartz/ALQ and quartz/DPP and double layer films quartz/DPP/ALQ.

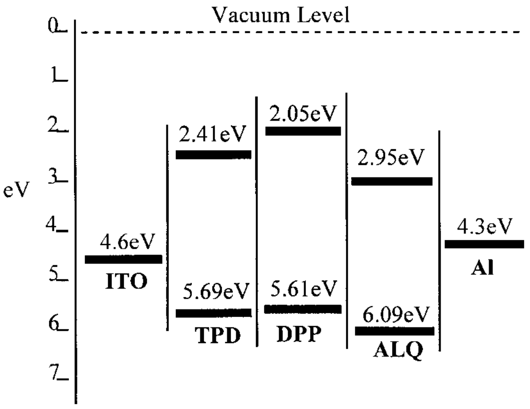


Fig. 6 The energy level diagram of the ITO/TPD/DPP/ALQ/Al device. The IPs of TPD and DPP were determined by film state CV. The EA of ALQ was determined as evaporated film on ITO by photoemission spectroscopy with a laser beam line 4B9B, which is consistent with that in references 17 and 18. The EAs of TPD and DPP and the IP of ALQ then were deduced from the first bands of their absorption spectra in the film state.

solution CV. We did not observe an apparent reductive CV peak in the negative potential region by using thin film ALQ on ITO as the working electrode. So, we use the value determined by photoemission spectroscopy for ALQ as evaporated thin film on ITO.

Electroluminescence

EL of the triple layer device, ITO/TPD/DPP/ALQ/Al was electric field strength (EFS) dependent. That is, a device with thinner organic layers exhibited blue emission from the DPP layer independent of the drive voltage; a device with thicker organic layers exhibited blue emission at high drive voltages but green emission at low drive voltages. Fig. 4 shows the EL spectra of the triple layer device under different drive voltages (the thickness of each of the organic layers was kept constant so the EFS would be proportional to the drive voltage). With increasing drive voltage, the EL emission gradually shifted from green to blue. At medium electric strength, the emission is at any wavelength from 520 to 470 nm. An excimer formation as mentioned before could possibly be the cause. However, the PL of thin film DPP did not show any new excimer emission except the emission at 470 nm. The possibility of an exciplex[10–12] formation at the interface between DPP and ALQ is also denied by the PL and absorption of the quartz/DPP/ALQ (the same as quartz/ALQ/DPP) double layer films. Fig. 5 shows the PL and absorption spectra of single layer quartz/DPP, quartz/ALQ and double layer quartz/DPP/ALQ. It is apparent that the wide PL emission peak in quartz/DPP/ALQ is the result of the overlap of DPP and ALQ emission, without any new exciplex emission. The absorption spectrum of the double layer films is also the overlap of the two independent single layers. Therefore an exciplex formation at the DPP/ALQ interface would also be impossible.

The reason for this kind of electric field strength dependent EL emission would be clear if the energy levels of each layer were compared. Fig. 6 shows the energy level diagram obtained by cyclic voltammetry (TPD and DPP) and photoemission spectra. In this diagram, the ionization potential of DPP is lower than that of TPD so holes would enter from TPD to the DPP layer freely after being injected from the ITO. The energy barrier (0.90 eV) for electrons being injected from the ALQ layer into the DPP layer is bigger than the energy barrier (0.48 eV) for holes being injected from the DPP layer into the ALQ layer. So at low EFS electrons would be blocked in the ALQ layer. When the EFS is sufficiently high, electrons would overcome this barrier height by a tunneling effect[13–16] and move into the DPP layer, then recombine with holes there and decay to emit light at 470 nm of DPP.

At a drive voltage of 18 V, the luminance obtained reached 2400 cd m^{-2}. At a current density of 1.27 mA cm^{-2}, the efficiency was 0.23 lm W^{-1}.

Conclusion

A new pyrazoline derivative molecule was synthesized and fabricated into an EL device. Its absorption, photoluminescence and electrochemistry both in solution and as thin film were studied. The absorption spectra cover the whole near-ultraviolet region. At higher concentrations, DPP exhibits a new excimer emission which derives from the face to face electron interaction of the pyrenyl group. This excimer or a possible exciplex formation is proved to be not the cause for the new emissions in EL at medium electric strength. These new EL emissions were explained by a tunneling effect based on the energy levels which were determined by thin film cyclic voltammetry.

References

1 C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, 1987, **51**, 913.

2 C. Adachi, S. Tokito, J. Tsutsui and S. Saito, *Jpn. J. Appl. Phys., Part 2*, 1988, **27**, 713.

3 J. H. Burroughs, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature* (*London*), 1990, **347**, 539.

4 I. D. Parker, *J. Appl. Phys.*, 1994, **75**, 1659.

5 P. S. Davids, I. H. Campbell and D. L. Smith, *J. Appl. Phys.*, 1997, **82**, 6319.

6 P. M. Borsenberger and L. B. Schein, *J. Phys. Chem.*, 1994, **98**, 235.

7 R. Young and J. Fitzgerald, *J. Phys. Chem.*, 1995, **99**, 4230.

8 T. Sano, T. Fujii, Y. Nishio, Y. Hamada, K. Siubata and K. Kuroki, *Jpn. J. Appl. Phys., Part 1*, 1995, **34**, 3124.

9 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, 1978.

10 D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, D.-K. Fu, T. M. Swager, A. G. Macdiarmid and A. J. Epstein, *Appl. Phys. Lett.*, 1997, **70**, 1644.

11 T. Granlund, L. A. A. Pettersson, M. R. Anderson and O. Inganas, *J. Appl. Phys.*, 1997, **81**, 8097.

12 K. Itano, H. Ogawa and Y. Shirota, *Appl. Phys. Lett.*, 1998, **72**, 636.

13 L. S. Hung, C. W. Tang and M. G. Mason, *Appl. Phys. Lett.*, 1997, **70**, 152.

14 F. Li, H. Tang, J. Anderegg and J. Shinar, *Appl. Phys. Lett.*, 1997, **70**, 1233.

15 G. E. Jabbour, Y. Kawabe, S. E. Shaheen, J. F. Wang, M. M. Morrell, B. Kippelen and N. Peyghambarian, *Appl. Phys. Lett.*, 1997, **71**, 1762.

16 H. Cao, X. C. Gao, Jin Zhai, C. H. Huang, B. W. Zhang and Y. Cao, *Synth. Met.*, 1998, **96**, 191.

17 E. Aminaka, T. Tsutsui and S. Saito, *J. Appl. Phys.*, 1996, **79**, 8808.

18 H. Suzuki and S. Hoshino, *J. Appl. Phys.*, 1996, **79**, 8816.

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