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Efficient green electroluminescence of pure chromaticity from a polycyclic aromatic hydrocarbon

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A new highly fluorescent material with a condensed aromatic ring, 7-naphthylbenzo[*a*]perylene (pNNA), was synthesized for application in organic electroluminescent devices (OELDs). The fluorescent quantum yield of this material in a 1×10^{-5} M solution of dichloromethane approached unity. OELDs have been fabricated with a configuration of ITO/NPB/AlQ–pNNA/Mg–Ag (ITO: indium tin oxide, NPB: *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine and AlQ is tris(8-hydroxyquinolinato)aluminium(III)). The device showed strong green emission with a narrow peak at 542 nm. When a mixture of pNNA and AlQ (1 : 400) was deposited from a single source, the electroluminescent efficiency of the devices reached 6.5 cd A^{-1} at 20 mA cm^{-2} and 7.8 V. A brightness of 15 000 cd m^{-2} was achieved at a driving voltage of 11 V.

1. Introduction

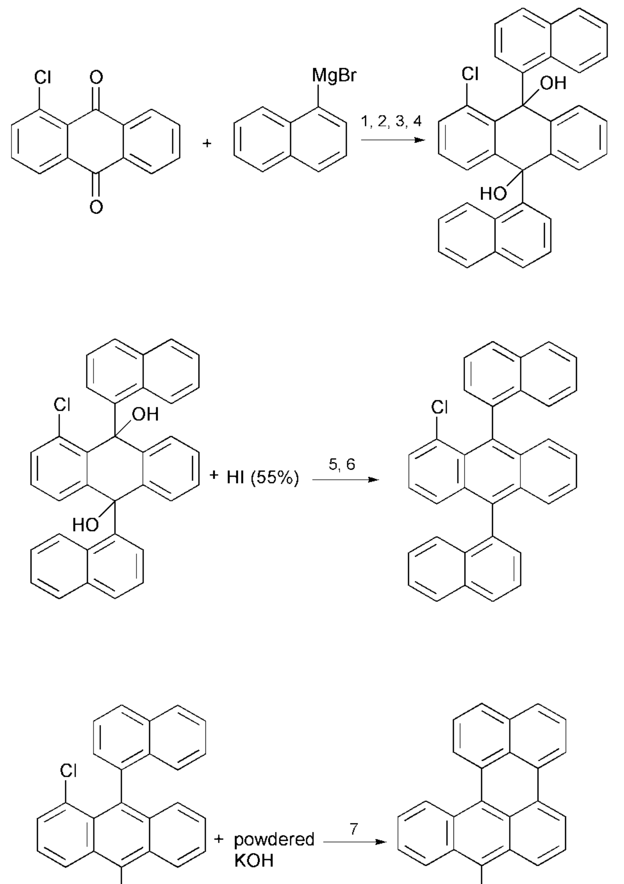
Organic electroluminescent devices (OELDs) have been widely studied in recent years.[1–3] OELDs are attractive especially for applications as flat panel displays (FPD). They have a number of advantages over other display technologies, such as low driving voltage, high brightness, large view angle, *etc.* To obtain high-performance OELDs with a low carrier injection barrier, high electroluminescence (EL) efficiency, and long life time, materials design and device configuration are both important considerations. It is desirable that the organic materials possess the following properties: good carrier transport properties, good stability, high photoluminescence (PL) quantum yield, suitable ionization potential (IP) and/or electron affinity (EA). Thus, the synthesis of highly fluorescent and stable materials that can be utilized in OELDs is one of the most important research areas in this field.

Some polycyclic aromatic hydrocarbons (PAHs) have very high PL quantum yield and have thus been used in OELDs.[4–9] The pure hydrocarbon conjugated structure of the compounds intrinsically determines their relatively high carrier transport abilities. Meanwhile, most of them are highly luminescent and relatively stable. It is thus considered that the PAH compounds may have special importance for OELD applications.

In this work, we synthesized a new PAH compound, 7-naphthylbenzo[*a*]perylene (pNNA), for use in OELDs. Both the photoluminescence and electroluminescence properties of PAH have been studied. The pNNA-doped devices at various concentrations were fabricated and the optimal device configuration was determined.

2. Experimental

7-Naphthylbenzo[*a*]perylene (pNNA) was prepared from 1-chloroanthraquinone and 1-bromonaphthalene following the procedure described in the literature,[10] except that different starting material and solvent were used. The synthesis is schematically shown in Scheme 1. First, the starting material 1-chloroanthraquinone was condensed with 1-naphthylmagnesium bromide, which was freshly prepared from 1-bromonaphthalene and



Scheme 1 Synthesis of pNNA. *Reagents and conditions*: 1. reflux, 2 h; 2. pour into dilute HCl–ice; 3. sodium dithionite to digest; 4. 1,2,4-trichlorobenzene to recrystallize; 5. reflux, 15 min; 6. wash with acetic acid–benzene; 7. quinoline, reflux, 45 min.

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magnesium turnings. Instead of ether and benzene, tetrahydrofuran (THF) was used as solvent. Second, the resulting diol was reduced by hydrogen iodide to the corresponding anthracene. Finally, by heating the product from step two with potassium hydroxide in quinoline, pNNA was obtained. This compound was further purified by column chromatography using silica gel as column material and hexane–THF as eluant, and the characterization data are as follows: melting point: 179.9–180.3 °C; MS: *m*/*z* 428.3 (M^+); Calc. for $C_{34}H_{20}$: C: 95.3%, H: 4.7%. Found: C: 95.5%, H: 4.8%; ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.90 (d, 1H), 8.38 (dd, 2H), 8.19 (d, 1H), 8.10 (d, 1H), 8.04 (d, 1H), 7.85 (dd, 2H), 7.74 (m, 1H), 7.64 (dd, 2H), 7.57 (m, 1H), 7.50 (m, 2H), 7.38 (m, 1H), 7.31 (m, 2H), 7.24 (m, 2H), 7.16 (d, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 136.7, 134.6, 134.5, 134.1, 133.6, 132.9, 131.4, 131.4, 131.2, 130.1, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 127.7, 127.6, 127.4, 127.3 (2C), 126.9, 126.5 (2C), 126.4, 126.4, 126.4, 126.2, 125.9, 125.9, 125.8, 121.0, 120.6.

The photoluminescence and absorption spectra of pNNA were measured respectively with a Perkin–Elmer LS50 fluorescence spectrophotometer and a Perkin–Elmer Lambda 2S UV-Visible spectrophotometer in a dichloromethane solution containing 1×10^{-5} M pNNA.

The chemical structures of the organic materials used in device fabrication are shown in Fig. 1. Devices with various doping concentrations of pNNA in an AlQ matrix were fabricated with a configuration of glass/indium tin oxide (ITO: 30 Ω/□)/NPB (700 Å)/pNNA-doped AlQ (350 Å)/AlQ (350 Å)/M–Ag (2000 Å; mass ratio of Mg to Ag is 10 : 1). The dopant concentration in weight was 0.5, 1, 2, and 4%, respectively. Generally, it is difficult to achieve a dopant concentration of less than 0.5% using the conventional co-evaporation method. To fabricate devices with extremely low dopant concentrations, we adopted a new approach that involves using a mixture of pNNA and AlQ premixed to a desired concentration as the source in one evaporator. The devices utilizing such a mixed source of pNNA and AlQ adopted a structure of glass/indium tin oxide (ITO: 30 Ω/□)/NPB (700 Å)/pNNA mixed with AlQ (350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å). The mixture ratio was 1 : 200, 1 : 400, 1 : 800, and 1 : 1200 in the evaporator source. Here, NPB is *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine and AlQ is tris(8-hydroxyquinolinato)aluminium(III). The ITO glass substrate was cleaned with detergents and deionized water, and dried in an oven for about two hours. Then it was treated with UV–ozone for 25 minutes before loading into a deposition chamber. NPB, AlQ–pNNA and AlQ films were sequentially deposited onto the ITO substrate at a pressure around 1.0×10^{-5} mbar. The pressure during metal deposition was below 9.0×10^{-6} mbar. The current–voltage–luminance characteristics and EL spectra were measured with a computer-controlled DC power supply and a Spectrascan PR650 photometer at room temperature. The emission area of the devices is 0.1 cm^2, as defined by the overlapping area of the anode and cathode.

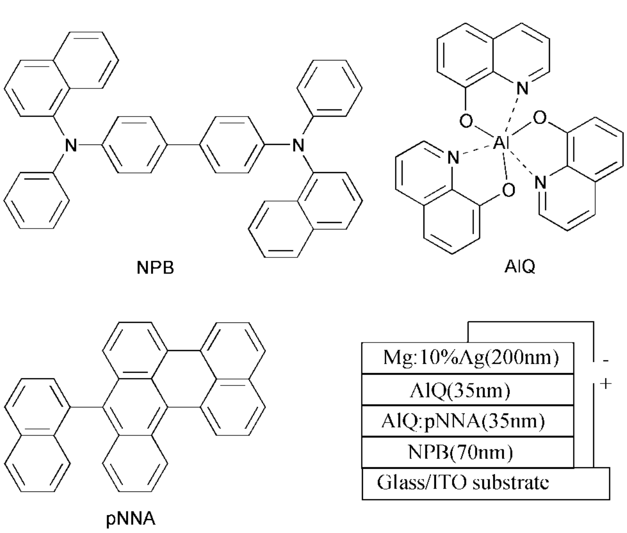

Fig. 1 Materials used in device fabrication.

3. Results and discussion

Fig. 2 shows the absorption and PL spectra of a 1×10^{-5} M pNNA solution in dichloromethane, and the EL spectrum of an undoped reference device having a structure of ITO/NPB (700 Å)/AlQ (700 Å)/Mg–Ag (2000 Å), which was recorded at current density of 20 mA cm^{-2}. The absorption spectrum of pNNA exhibits three peaks at 519, 481 and 454.8 nm respectively, while the emission spectrum has two peaks at 540 and 573 nm (shoulder). The relatively small Stokes shift of 21 nm is attributed to the structural rigidity of the pNNA molecule. It can be seen from Fig. 2 that the EL spectrum of AlQ covers the full width of the first absorption peak of pNNA. Thus, Förster resonance energy transfer from AlQ to pNNA is expected to be efficient if pNNA is doped into the AlQ matrix.

Fig. 3 shows the EL spectra of the pNNA devices having the structure of ITO/NPB (700 Å)/AlQ: pNNA (350 Å)/AlQ (350 Å)/Mg: Ag (2000 Å), which was recorded at current density of 20 mA cm^{-2}. The dopant concentration was varied from 0.5% to 4% by weight. The result from the undoped reference device was also included for comparison. Compared with the PL emission in Fig. 2, the EL emission peaks of the doped devices are almost identical to the PL peaks in solution. This confirms that the EL emission of the three doped devices indeed comes from pNNA molecules. The full width at half maximum of the pNNA EL emission peak is about 60 nm, which is much narrower than the emission peak of AlQ. Even at a dopant concentration as low as 0.5%, the emission of AlQ is totally invisible, indicating a thorough energy transfer from AlQ to pNNA.

As is well established, there are two mechanisms for energy transfer in OELDs. One is the Förster energy transfer, which is facilitated by the overlap of the emission peak of the host with the absorption peak of the dopant. Usually the effective distance for this kind of energy transfer is large and typically in

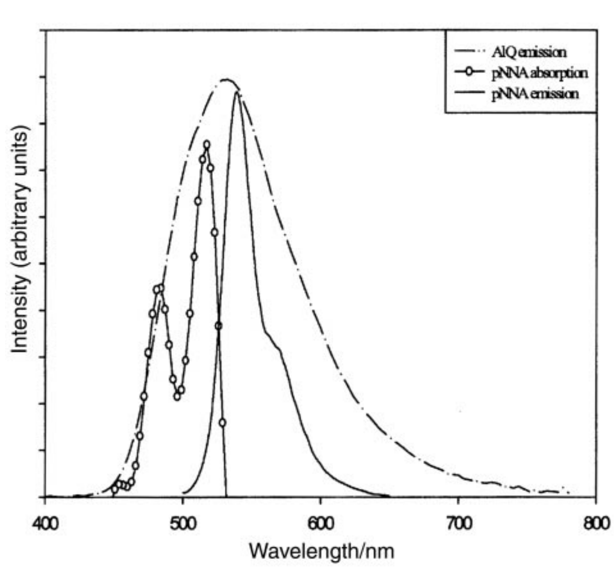

Fig. 2 Absorption and photoluminescence spectra of pNNA in dichloromethane (1×10^{-5} M), and the EL spectrum of an undoped reference device having a structure of ITO/NPB (700 Å)/AlQ (700 Å)/Mg–Ag (2000 Å).

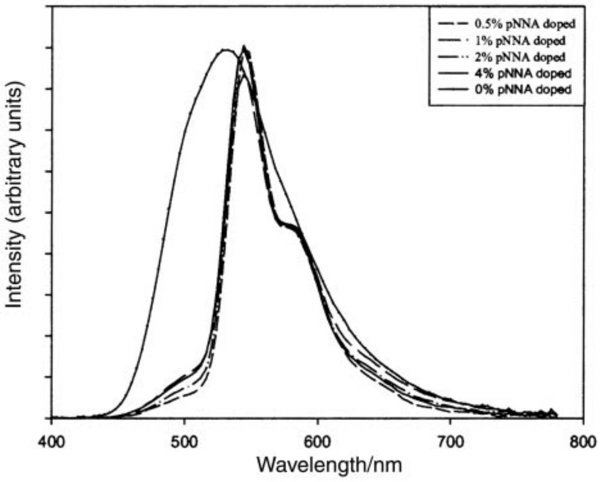

Fig. 3 EL spectra of the 0%, 0.5%, 1%, 2%, and 4% pNNA-doped devices having the structure of ITO/NPB (700 Å)/AlQ/pNNA (350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å).

the range of 10–100 Å. The other mechanism is the Dexter energy transfer. This usually requires a close proximity between the molecular orbitals of the donor and the acceptor molecules. The interaction distance is typically of the order of several Å. Thus, Dexter energy transfer is only efficient when the acceptor concentration is high in the donor (>5%). In the present devices, the Förster energy transfer is expected to be dominant, so that a high dopant concentration should not be required due to the relatively large interaction distance of Förster energy transfer. As a result, the effect of concentration quenching can be reduced because only a small dopant concentration is needed. Furthermore, as the pNNA emission is much narrower than that of the AlQ (Fig. 3), the devices doped with pNNA have better color purity than the reference undoped AlQ device.

The efficiency characteristics of the devices doped with 0.5%, 1%, 2%, and 4% pNNA are shown respectively in Fig. 4. In this series of doped devices, the device efficiency increases with decreasing dopant concentration. As mentioned above, this phenomenon is attributed to the good overlap between the absorption spectrum of the dopant and the emission spectrum of the host, which leads to very efficient energy transfer from host to dopant. As concentration quenching is expected to diminish with decreasing dopant concentration, thus we suspect that a dopant concentration of less than 0.5% may lead to further efficiency improvement. However, in the conventional way of device fabrication, it is normally difficult to accurately control the dopant concentration at a value less than 0.5%. In our work, we introduce a novel method by which very small (<0.5%) dopant concentrations can be consistently achieved. In this method, pNNA and AlQ are mixed together with a desired ratio, and the mixture thus prepared is thermally evaporated in a single source.

The current efficiency of the devices fabricated from the "mixed source" is shown in Fig. 5. Remarkably, the performances of the devices were significantly improved compared to the devices prepared from the "separate source". The EL spectra of these "mixed source" devices are the same as those of the "separate source" devices. The current efficiency of 1 : 200 pNNA "mixed source" device is comparable to the 0.5% pNNA "separate source" device. Furthermore, the current efficiency of the "mixed source" device increased with decreasing concentration in the mixed source or mixture. When pNNA in the mixture is reduced to 1 : 400, the current efficiency became saturated at around 6 cd A^{-1} at the driving voltage of 7.8 V and current density of 20 mA cm^{-2}. When the pNNA concentration in the mixture further decreased, the current efficiency began to drop. This can be attributed to the effect of decreasing luminescent centers.

Repeated depositions from a single "mixed source" gave reproducible results.

The luminance–voltage and current density–voltage characteristics of the device having the configuration of glass/ITO/NPB (700 Å)/pNNA mixed with AlQ (1 : 400, 350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å) are shown in Fig. 6. At about 12 V, the luminance reaches 16 000 Cd m^{-2} with a current density of 260 mA cm^{-2}. Together with Figs. 4 and 5, performance of the devices using the material concerned can be clearly seen.

Fig. 7 shows the EL spectra of device with a structure of glass/ITO/NPB (700 Å)/pNNA mixed with AlQ (1 : 800, 350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å) at different applied voltages. The EL spectra at different driving voltages are almost the same, even at the low dopant concentration (1 : 800). This indicates that the critical concentration[11] for Förster energy transfer from AlQ to pNNA is very low. This is attributed to the overlap of spectra between the emission of the host (AlQ) and the absorption of the dopant (pNNA).

4. Conclusions

A condensed polycyclic aromatic compound, 7-naphthylbenzo-[*a*]perylene (pNNA), was synthesized. This compound has a high fluorescence quantum yield of almost 100% in solution as measured using quinine sulfate as reference according to method in literature.[12] OELD fabricated from a mixture of pNNA and AlQ exhibited an EL efficiency of 6.5 cd A^{-1} at

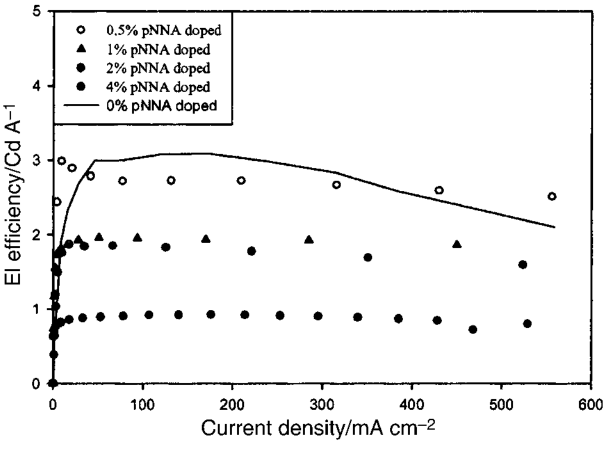

Fig. 4 EL efficiencies of the 0%, 0.5%, 1%, 2%, and 4% pNNA-doped device having the structure of ITO/NPB (700 Å)/AlQ–pNNA (350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å).

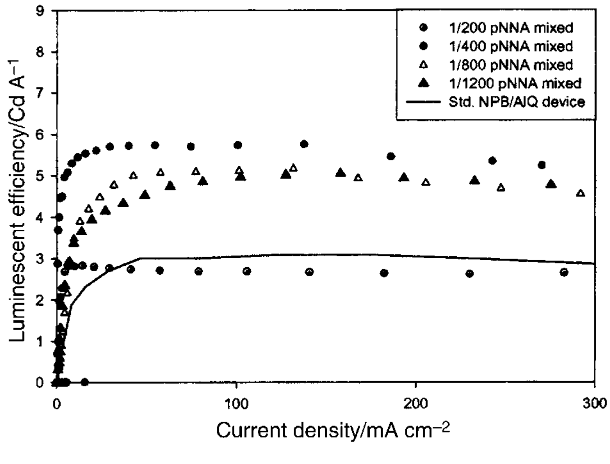

Fig. 5 EL efficiencies of the 1 : 200, 1 : 400, 1 : 800, and 1 : 1200 pNNA "mixed source" devices with a structure of glass/ITO/NPB (700 Å)/pNNA mixed with AlQ (350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å).

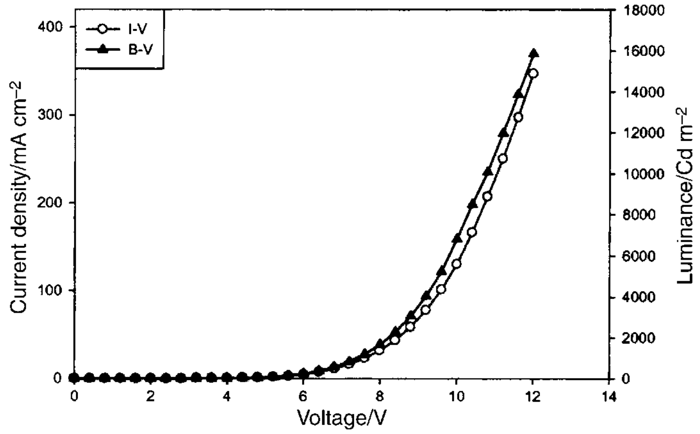

Fig. 6 The luminance–voltage and current density–voltage characteristics of a device having the structure glass/ITO/NPB (700 Å)/pNNA mixed with AlQ (1 : 400, 350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å).

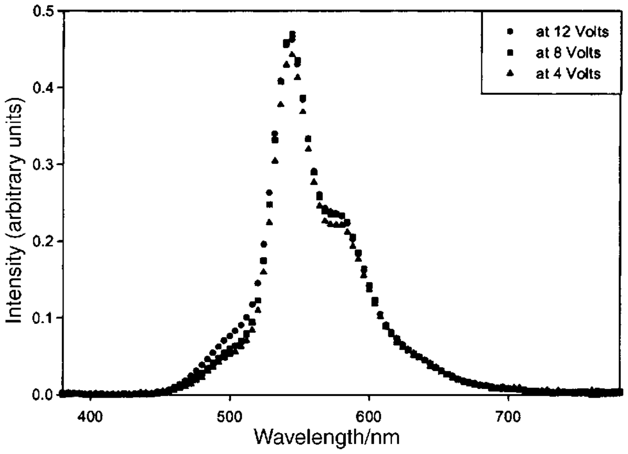

Fig. 7 EL spectra of device with a structure of glass/ITO/NPB (700 Å)/pNNA mixed with AlQ (1 : 800, 350 Å)/AlQ (350 Å)/Mg–Ag (2000 Å) at different applied voltages.

20 mA cm^{-2} and a driving voltage of 7.8 V. The pNNA "mixed source" device is far superior to the prototypical NPB/AlQ bilayer device both in terms of power efficiency and color purity. The stable conjugated system, high luminescence, and narrow emission peak of the compound pNNA make it a promising material for OELDs applications.

Acknowledgements

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