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A new pyridylamine for blue light electroluminescent devices

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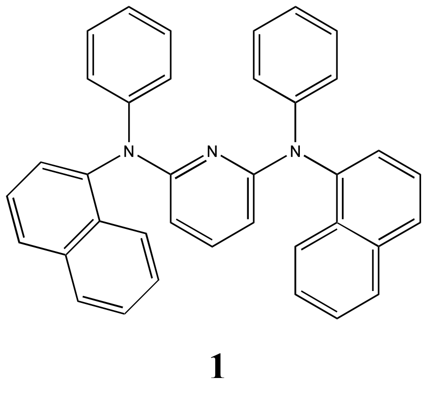
Abstract—The new pyridylamine, *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-2,6-diaminopyridine (NPP), in which the nitrogen atoms form a linear array, was synthesized by the reaction of 2,6-dibromopyridine with *N*-phenyl-1-naphthylamine. This compound emits an intense blue color ($\lambda = 443$ nm, $\Phi_f = 0.74$) upon irradiation by UV light and is suitable for use as an emitting layer in an electroluminescent device. © 2001 Elsevier Science Ltd. All rights reserved.

Investigations on synthesizing new blue luminous materials for applications in electroluminescent (EL) displays have attracted great attention from researchers during recent years.[1] The colors and high luminescence as well as low driving voltage of organic EL devices are particularly suited for applications in flat panel displays.[2] Although blue EL emitters are important in developing full-color EL display panels, they are rare and inefficient thus far. Numerous aromatic amines have been developed as hole transport layers (HTL) in organic EL devices. Those that are widely used in current organic EL research include *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)(1,1′-biphenyl)-4,4′-diamine (TPD), *N*,*N*,*N*′,*N*′-tetrakis(4-methylphenyl)(1,1′-biphenyl)-4,4′-diamine (TTB), and *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB).[1e] During our investigation of pyridylamine chemistry, we found that the compound, *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-2,6-diaminopyridine, NPP, in which the nitrogen atoms form a linear array, has potential application in electroluminescent devices. In this paper, we report the preliminary results of the synthesis and structure and light-emitting properties of NPP.

The white compound (*N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-2,6-diaminopyridine), NPP, **1**, was isolated in ca. 55% yield from the reaction of 2,6-dibromopyridine with *N*-phenyl-1-naphthylamine and potassium carbonate.[3] The formula of this compound was determined by ^{1}H NMR, elemental analysis and X-ray crystallography.[4] Crystals of NPP conform to the space group $P\bar{1}$ with two independent molecules in each asymmetric unit which are enantiomers of each other. Fig. 1 shows a representative ORTEP diagram for one of the two independent molecules. The molecule adopts a conformation with C_1 symmetry, and the phenyl and naphthyl groups of the two *N*-phenyl-1-naphthylamine wings are oriented *trans* to one another. The two naphthyl rings are roughly perpendicular to the central pyridine ring. The average N–C distance outside the pyridine ring, 1.423 Å, is longer than that inside the pyridine ring which is 1.339 Å, but shorter than the average N–C single bond distance which is 1.530 Å. We thus note that the N–C bond outside the pyridine ring possesses partial double-bond character.[5] This is verified by the fact that the average C–N–C angle outside the pyridine ring is 120°. To the best of our knowledge, NPP is the first example of a chiral compound of the type $Ar_2Z(Ar)ZAr_2$ in which Z is not a chiral center. A view of the packing diagram of NPP shows that there are no π–π interactions and no intermolecular hydrogen bond-



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Keywords: pyridylamine; luminescence; electroluminescent device.

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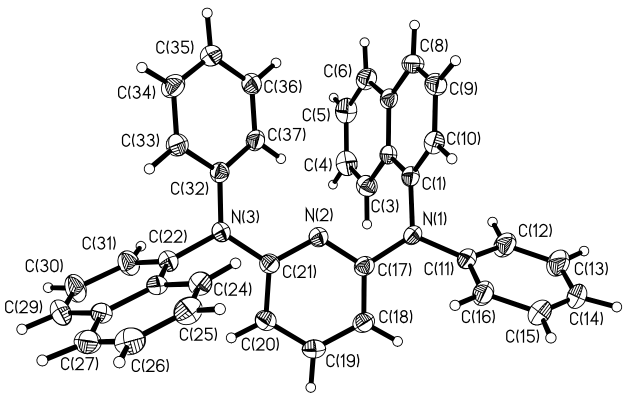

Figure 1. An ORTEP diagram of NPP.

ing between the molecules. Therefore, the UV–vis spectra of NPP in the solid-state is almost identical to the one measured in solution.[6] This compound is remarkably stable towards air in the solid state as well as in solution. This compound is also thermally stable. It melts at 220°C without decomposition and can be sublimed at ca. 150°C and 0.01 mmHg. Absorption and photoluminescence (PL) spectra were studied for solutions and for thin films obtained by vacuum deposition of NPP onto quartz substrates. The most striking feature is that NPP emits an intense blue color upon irradiation by UV light. The emission maximum in the solid is at $\lambda=443$ nm, and the full width at half maximum is 71 nm. The dichloromethane solution of NPP emits at 440 nm and the PL quantum yield Φ_f was estimated to be 0.74, relative to that of rhodamin.[7] It is noted that the starting compounds, dibromopyridine and *N*-phenyl-1-naphthylamine do not have any observable luminescence both in solution and solid states. Condensation of these two compounds produced NPP, which not only shows a drastic shift of the emission band but also an increase in the emission intensity. This is most probably due to the fact that both π systems of the dibromopyridine and the *N*-phenyl-1-naphthylamine have been extended,[8] and the product NPP shows neither π–π interactions nor intermolecular hydrogen bondings between molecules.

A triple-layer organic light-emitting diode (OLED) was fabricated using NPP as the emitting layer, indium tin oxide (ITO) as the anode material and an evaporated Mg alloy with a small amount of silver (ca. 10:1) as the cathode.[9] Moreover, the electron transport material (1,3,4-triazole, TAZ)[10] and the hole transport material (*N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine, NPB)[11] were deposited. The cell structure [MgAg/TAZ/NPP/NPB/ITO] is schematically shown in Fig. 2. The emitting layer was fabricated by vacuum deposition of NPP (200°C, 10^{-7} torr) onto the interface between the hole transport layer (HTL) and the electron transport layer (ETL) to form a thin homogeneous film. The film thickness was controlled to be 300 Å. The Mg/Ag cathode (thickness about 1500 Å) was vacuum deposited onto the top of the electron transport layer (ETL). The substrate was kept at room temperature during the deposition and the active area of the LED was 3×3 mm^2. When the triple-layer LED was forward biased with the ITO electrode at positive polarity, blue EL was observed. Fig. 3 shows the EL spectrum, which exhibits a blue emission with three fine peak wavelengths at 412, 420 and 436 nm, respectively. The splitting of the band might arise from the effect of intramolecular charge transfer (ICT).[12] Fig. 4 shows the brightness–voltage and current–voltage curves of the triple-layer LED, which shows brightness of 1 cd m^{-2} at a driving voltage of 7.2 V with a current density of 1.8 mA cm^{-2}. Its EL efficiency was estimated to be 0.22 lm/W with a yield of 0.9 cd/A.

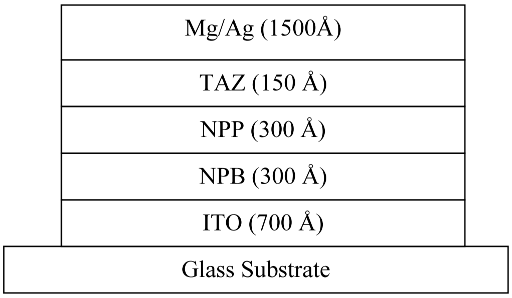

Figure 2. The cell structure of the triple-layer LED.

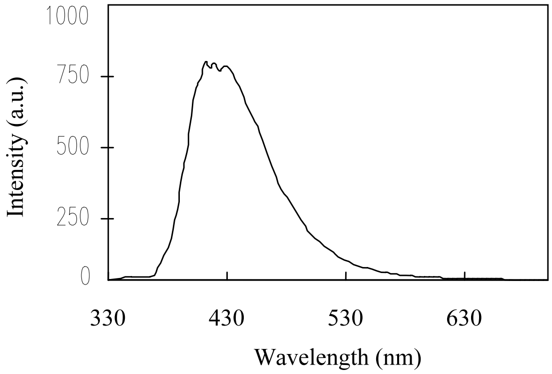

Figure 3. The EL spectrum of the triple-layer LED.

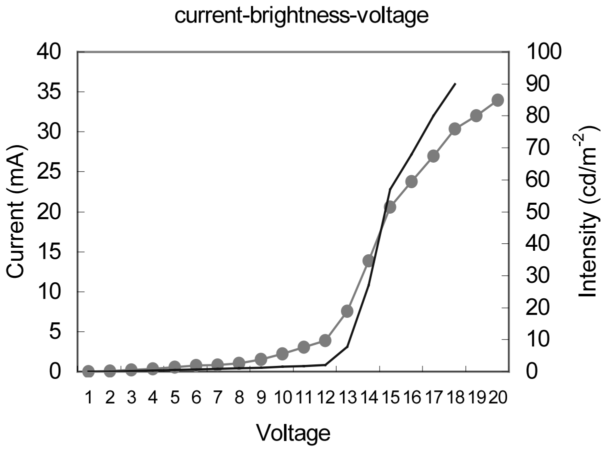

Figure 4. The brightness–voltage and current–voltage characteristics of the triple-layer LED: (solid line) brightness voltage curves, (dotted line) current voltage curves.

In summary, a new blue electroluminescent compound of pyridylamine, NPP, has been synthesized and structurally characterized. This new material exhibits an intense fluorescence at 443 nm in the solid-state and also forms dense and pinhole-free films. Preliminary studies indicated that the present triple-layer device is air-stable. Because of its high thermal stability and high photoluminescence quantum yield, NPP and its related pyridylamine compound may have possible applications in electroluminescent devices.

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3. A solution of 2,6-dibromopyridine (2.37 g, 10 mmol), *N*-phenyl-1-naphthylamine (5.48 g, 25 mmol), potassium carbonate (4.14 g, 30 mmol), and copper powder (1.6 g, 25 mmol) in 10 ml of anhydrous DMF was refluxed for 24 h. The solution was then cooled down to rt and extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated in vacuum. The product, NPP, was purified by chromatography. Yield 2.82 g (55%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.91 (d, $^3J_{H-H} = 8$ Hz, 2H, *pyridyl*), 6.86 (m, 1H, *phenyl*), 6.98 (m, 9H, *phenyl*), 7.09 (t, $^3J_{H-H} = 8$ Hz, 1H, *pyridyl*), 7.35–7.93 (m, 14H, *naphthyl*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.1, 117.6, 119.6, 120.2, 120.7, 122.9, 124.4, 124.6, 124.9, 125.0, 125.1, 125.2, 125.6, 125.8, 126.1, 126.2, 126.4, 126.5, 126.7, 127.0, 128.9, 129.2, 129.4, 129.6, 129.7, 130.4, 131.6, 132.0, 135.5, 137.1, 139.9, 142.6, 144.9, 145.1, 150.8, 150.9. IR (KBr, cm^{-1}): 1603 (s), 1571 (s), 1494 (s), 1438 (s), 1389 (s), 1361 (m), 1284 (s), 1157 (m). Calcd for $C_{37}H_{27}N_3$ (MW = 513.64) C, 86.52; H, 5.29; N, 8.18. Found C, 86.67; H, 4.80; N, 8.14. MS (70 eV): *m*/*z*. 513 (M^+, 2), 219 (100), 204 (10), 189 (8), 165 (8), 140 (10), 126 (15), 115 (30), 109 (28), 77 (20). UV (CH_2Cl_2): λ nm (ε). 344 (4.5×10^5), 282 (2.6×10^5). Fluorescence (CH_2Cl_2): λ nm (Φ_f). 440 (0.74).
4. Crystal data: $C_{37}H_{27}N_3$, $M = 513.62$, triclinic, space group $P\bar{1}$, $a = 10.898(1)$, $b = 12.456(1)$, $c = 20.315(1)$ Å, $\alpha = 99.782(1)$, $\beta = 96.463(1)$, $\gamma = 90.775(1)°$, $V = 2698.8(3)$ Å^3, $Z = 4$, $D_c = 1.264$ g cm^{-3}, $\mu = 0.074$ mm^{-1}, 13246 reflections measured, no. of unique reflections = 9015 ($R_{int} = 0.0246$), no of parameters = 938, $R_1 = 0.0599$ and $wR_2 = 0.1226$ with $I > 2\sigma(I)$. The diffraction data was collected on a Siemens CCD diffractometer, which was equipped with graphite-monochromated Mo Kα (Kα = 0.71073 Å) radiation. Structure refinements were carried out using the SHELXTL software package.[13] The crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC165485. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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