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Organic Multilayer White Light Emitting Diodes

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Simple, low-power, electroluminescent (EL) devices based on thin films of organic materials are promising candidates for a host of applications, such as flat panel displays and backlights. The need for white light emitting diodes (LEDs) and backlights has spurred interest in the preparation of white light emitting devices so that red, green, and blue would be conveniently available from one device.[2,3] The most stable LEDs use the efficient green emitter, tris(8-hydroxyquinoline)aluminum (AlQ), and a hole transporter such as *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD).[4] The green/red emission in such devices has been enhanced by incorporating lower energy dopants.[4] However, increased blue output cannot readily be achieved in a similar manner. We report new bright white and mixed color displays that are stable and exhibit fairly good quantum efficiencies. This was achieved by modifying the double-layer TPD/AlQ device structure to include a new triaryl-substituted oxazole blue/green emitter layer and the red fluorescent dye DCM1 as a dopant in a second AlQ layer. The physics of our device operation is markedly different from that recently reported by Kido and co-workers.[5] The blue emission in our devices comes from a triaryloxazole instead of from the hole transporter, TPD. This difference not only provides another degree of freedom in terms of device construction, but, more importantly, it should also give an advantage in terms of device stability, since exciton formation and subsequent emission from TPD decreases device longevity.[6]

The TPD/AlQ device structure consists of two layers of organics sandwiched between electrodes (Figure 1a). It is prepared by sequentially depositing onto an indium−tin oxide anode (ITO) layer TPD (**1**, Figure 2), AlQ (**2**), and a low work function metal cathode such as aluminum. Doping the AlQ with small amounts of fluorescent dyes has been shown to lead to changes in the EL spectrum and to higher external quantum efficiency.[4]

The emission spectrum of AlQ is weak in the blue and red compared to green ($\lambda_{\max} = 540$ nm) and is not completely satisfactory for white LEDs. We have developed an alternate approach to white light LEDs that enhances blue emission and does not require a microcavity.[3] It involves using a new blue/green emitting compound that can be deposited between the AlQ and the diamine TPD (Figure 1b). It was our intention to broaden the emission profile of TPD/AlQ by first bolstering the emission of blue light and subsequently enhancing emission of the red component by adding a red emitting dye, if required.

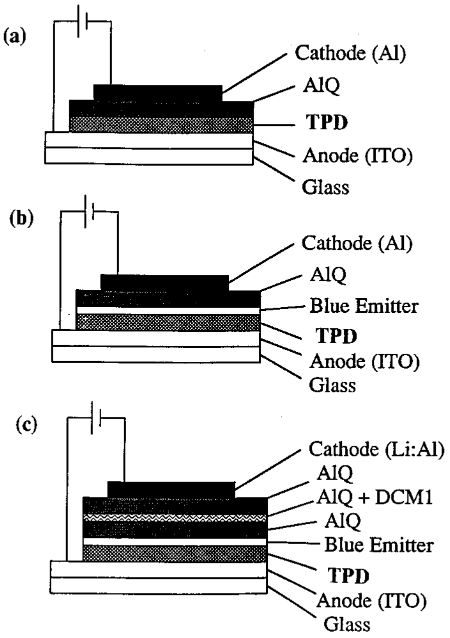

Figure 1.

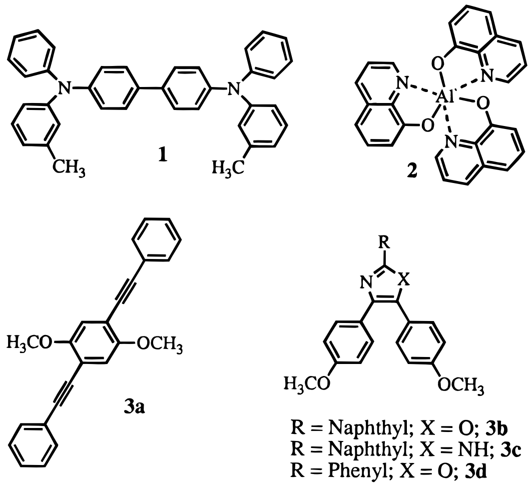

Figure 2.

Three new blue/green emitters, **3a−c** (Figure 2), and compound **3d**, synthesized from readily available starting materials using simple synthetic routes (one or two steps), were surveyed for this application. Compound **3a**[7] was prepared in one step by coupling 1,4-dibromo-2,5-dimethoxybenzene with phenylacetylene in the presence of bis(triphenylphosphine)palladium(II) chloride and cupric acetate in THF (see supporting information). The substituted oxazoles **3b**[8] and **3d**[9] were both prepared in a two-step sequence by first esterifying 4,4′-dimethoxybenzoin with the appropriate aryl acid chloride, followed by ring closure in refluxing glacial acetic acid with ammonium acetate (see supporting information). The substituted imidazole **3c**[10] was prepared similarly in a one-step reaction from 4,4-dimethoxybenzil and 1-naphthaldehyde using ammonium acetate (see supporting information). Preliminary characterization of the photoluminescence (PL) profiles of **3a−c** showed bright blue emission in dilute solution, with maxima at 460 nm [420 nm (s)], 445 nm, and 430 nm, respectively. For device applications, the compound must emit efficiently in the solid state, and it must also form stable homogeneous adherent films. For thin films (~800 Å thick) prepared by evaporation, only **3b** fulfilled both criteria ($\lambda_{\max(1)} = 440$ nm and $\lambda_{\max(2)} = 500$ nm). The imidazole **3c** forms excellent thin films but

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[4] Tang, C. W.; VanSlyke, S. A.; Chen, C. H. Chen *J. Appl. Phys.* **1989**, *65*, 3610.

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[6] Tang, C. W. Private communication.

[7] mp = 177−179 °C. Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36; O, 9.46. Found: C, 84.97; H, 5.26; O, 9.24.

[8] mp = 137−139 °C. Anal. Calcd for $C_{27}H_{21}NO_3$: C, 79.59; H, 5.19; N, 3.44; O, 11.78. Found: C, 79.40; H, 5.15; N, 3.31; O, 11.40.

[9] mp = 125−127 °C. Anal. Calcd for $C_{23}H_{15}NO_3$: C, 77.29; H, 5.36; N, 3.92; O, 13.43. Found: C, 77.33; H, 5.24; N, 3.85; O, 13.37.

[10] mp = 259−261 °C. Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.78; H, 5.46; N, 6.89; O, 7.87. Found: C, 79.72; H, 5.44; N, 6.77; O, 7.49.

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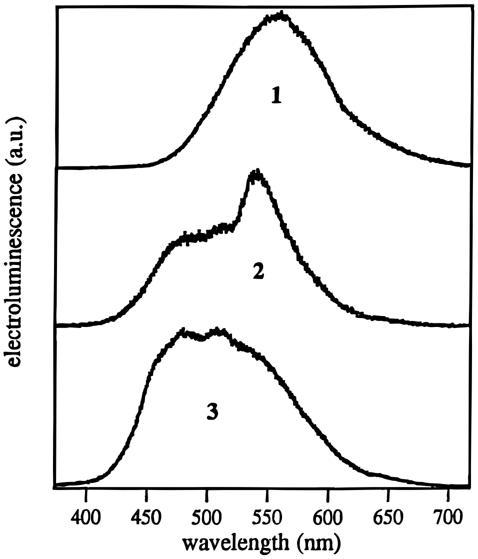

Figure 3. Device electroluminescence spectra. (1) TPD/AlQ; (2) TPD/oxazole **3b**/AlQ; (3) TPD/oxazole **3b**/AlQ/AlQ + DCM1/AlQ.

exhibits weak emission in the solid state ($\lambda_{\max} = 445$ nm), presumably due to self-quenching. While the linear species **3a** is chemically very stable in thin film form and emits strongly ($\lambda_{\max} = 460$ nm), it exhibits a propensity to crystallize after evaporation to form large crystals (> 500 Å). It is thought that organic solids that form large crystallites yield devices that perform poorly, because grain boundaries function as quenching sites. Oxazole **3d** also forms excellent films; however, it was specifically chosen so it would not emit in the blue (*vide infra*). Compounds **3b**−**d** presumably form good films, because the noncoplanar conformation of the pendant aryl rings hinders crystallization. This reasoning is corroborated by CAChe molecular modeling results, which predict that the pendant aryl rings in **3b**−**d** are, indeed, noncoplanar with the oxazole heterocycle in the minimum energy confirmation.[11] Such deportment is also inherent in TPD, which forms amorphous films,[12] while AlQ has been reported to be microcrystalline (<500 Å).[4]

The three-layer device structure with **3b** as the blue/green emitter is depicted in Figure 1b. This device exhibits a significantly broader EL spectrum, spanning the range 400−650 nm (Figure 3), than does TPD/AlQ, due to enhanced blue emission.[13] This device architecture allows exciton recombination to occur in more than one layer. In the TPD/AlQ device, hole and electron recombination occurs in the AlQ layer, presumably because of the energy levels and the transport properties of AlQ and TPD. The output spectrum is fairly broad and peaks in the green at 540 nm. In the new device, the green emission comes from both AlQ and **3b**, but nearly all of the blue emission comes from the latter. We are confident that the blue emission does not come from TPD, because substitution of **3b** by **3d**, a species which is almost identical and does not emit visible light, gives devices that lack the blue emission component. As the thickness of the oxazole (**3b**) layer is increased, the electroluminescence spectrum shifts toward blue. Increasing the thickness of **3b** beyond 150 Å causes no appreciable change in the spectrum but reduces efficiency. In addition to serving as one of the emitting layers, **3b** also transports one of the carriers preferentially.

To get as close as possible to white light emission, the device architecture was modified further (Figure 1c) to increase the contribution of the red component by incorporating small amounts of the red emitting dye DCM1 into a second AlQ layer.[4] The amount of red light was modulated by incorporating an undoped AlQ layer of thickness 100−300 Å between oxazole **3b** and the doped AlQ (+DCM1) layer and by varying the dopant concentration from 0.3 to 0.5%. The whitest EL spectrum (Figure 3) was obtained for a 300 Å AlQ filler and a 200 Å doped AlQ (0.5% DCM1) layer capped by a 200 Å thick AlQ undoped layer (Figure 1c).

Finally, in order to make a realistic and quantitative comparison between various white light emitting devices, it is imperative to specify the color of the emitted light in photometric terms, as standardized by the Commission Internationale de l'Eclairage (CIE).[14] When the radiometric EL spectra are converted into chromaticity coordinates on a CIE diagram, the TPD/AlQ device (CIE 0.39, 0.56) shows movement from green in the basic system, to blue−green for TPD/oxazole **3b**/AlQ (0.28, 0.46), and then toward white for TPD/oxazole **3b**/AlQ/AlQ + DCM1/AlQ (0.32, 0.41). The CIE coordinates for absolute white are (0.33, 0.33). The luminescence intensity and external quantum efficiency of the devices are as high as 4000 cd/m^2 and >0.5%, respectively, at an operating voltage of 15 V using a double-layer Li:Al cathode. Most importantly, preliminary measurements indicate that the *stability*,[15] *operating voltage*, and *quantum efficiencies* of these new devices are comparable to those of the TPD/AlQ device. Furthermore, the combination of EL materials reported here could also be successfully employed in microcavity LEDs to selectively enhance individual or multiple colors that lie within the emission band. This would involve changing the thickness of a microcavity containing a polyimide or a silicon nitride filler layer to utilize Fabry−Perot cavity effects (for microcavity LEDs), allowing red, green, and blue emission to be obtained.

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Supporting Information Available: Synthesis and characterization of **3a**−**d** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[11] Computer Aided Chemistry molecular modeling program (Cache, Version 3.0; CAChe Scientific, 18700 NW Walker Rd., Bldg. 92-01, Beaverton, OR 97006). Compound **3b:** naphthalene group is twisted 20° out of the plane of the oxazole ring, and the two pendant anisole moieties are twisted 31° and 36.6°. For **3d**, the anisole groups are similarly twisted, and the phenyl group if coplanar (2°).

[12] Stolka, M.; Yanus, J. F.; Pai, D. M. *J. Phys. Chem.* **1984**, *88*, 4707.

[13] Typical thicknesses were TPD, 600 Å; oxazole **3b**, 150 Å; AlQ, 600 Å; Al, 2000 Å.

[14] *Colorimetry*; Central Bureau of the CIE: Vienna, 1986.

[15] Devices have a shelf-life of at least 9 months.