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White light emission from blends of blue-emitting organic molecules: A general route to the white organic light-emitting diode?

J. Thompson,[a] R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli, and R. Cingolani
National Nanotechnology Laboratory of INFM and Agilent Futures Laboratory, Dipartimento di Ingegneria dell'Innovazione, Universita' di Lecce, Via Arnesano, 73100 Lecce, Italy

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We show that all possible binary combinations of molecules from four different families of organics—a diamine derivative, *N*,*N*′-bis(3methylphenyl)-*N*,*N*′-diphenylbenzidine, an oxidiazole derivative, 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, a substituted thiophene dioxide, 2,5-bis(trimethylsilyl thiophene)-1,1-dioxide, and poly(9-vinylcarbazole)—produce white or near-white emission. We suggest that this is due to exciplex formation, and that this is likely to be a general phenomenon for blends of blue-emitting aromatic organics. This implies that films of spin-coated blends of blue-emitting organics represent a general, simple, and cheap route to white-emitting organic light-emitting diodes.
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Organic light-emitting diodes (LEDs) potentially represent a cheap route for display technology, and may also have applications in the lighting industry, for which the white light market is the largest. In general, to obtain white light emission, two or more colors must be combined, i.e., a high energy emitter (e.g., blue) and a relatively low-energy emitter (e.g., green/yellow). This can be done using a multilayer structure including two (or more) different emitting molecules, usually fabricated by sequential evaporation.[1,2] An alternative is to use a spin-coated blend of two (or more) soluble organics,[3] which is clearly advantageous from the perspectives of both cost and ease of fabrication. A problem with the latter method is that often the higher-energy emission will overlap with the absorption band of the low-energy emitting molecule, with the resulting Foerster transfer leading to emission only from the low-energy molecule.[3]

In this letter we suggest that, in fact, a general method to obtain white emission is to spin coat a blend of two organic molecules, *both* of whose individual emissions lie in the blue. We show that all possible binary combinations of four different blue emitting organic molecules, from four different families of molecules, produce white, or near-white emission.

The structures and photoluminescence spectra of the four materials are shown in Fig. 1. They were a diamine derivative, TPD, *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine, an oxidizaole derivative, PBD, 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, a substituted thiophene dioxide, STO, 2,5-bis(trimethylsilyl thiophene)-1,1-dioxide, and the poly-carbazole PVK, poly(9-vinylcarbazole). TPD, PBD, and PVK were obtained from Aldrich and used without further purification. STO was synthesized and purified as described in Ref. 4. Equimolar solutions were made of the oligomer: oligomer blends, while an (arbitrary) mass ratio of 10:1 was used for the polymer: oligomer blends. Toluene was used as the solvent for TPD and its blends, while dichloromethane was used for all others. Films were spin coated onto quartz glass substrates, and photoluminescence spectra excited by a He:Cd laser ($\lambda=325$ nm). UV/visible absorption spectroscopy was performed using a Varian/Cary spectrophotometer.

Photoluminescence spectra of the six blends are shown in Fig. 2. All the blends, with the exception of PVK/PBD show broadband emission in the visible range, dominated by peaks which cannot be assigned to the individual molecule

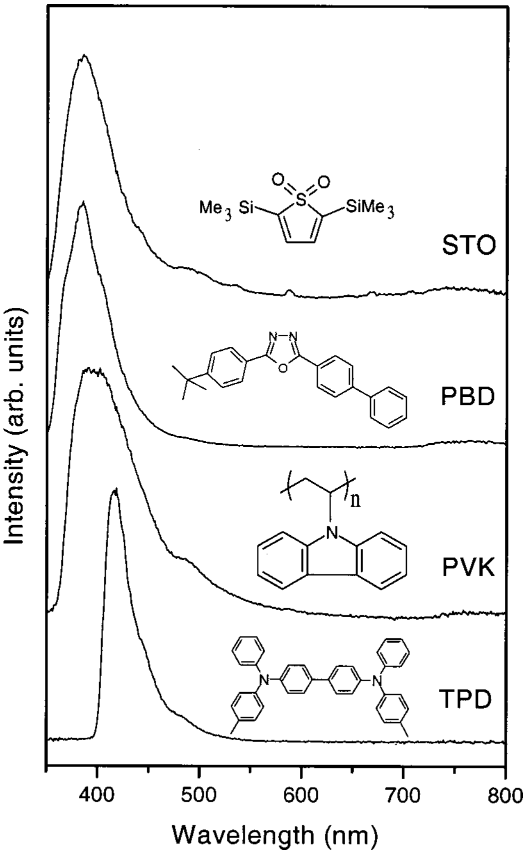

FIG. 1. Photoluminescence spectra in solution, and structures, of the molecules investigated are shown.

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[a] Author to whom correspondence should be addressed; electronic mail: julie.thompson@unile.it

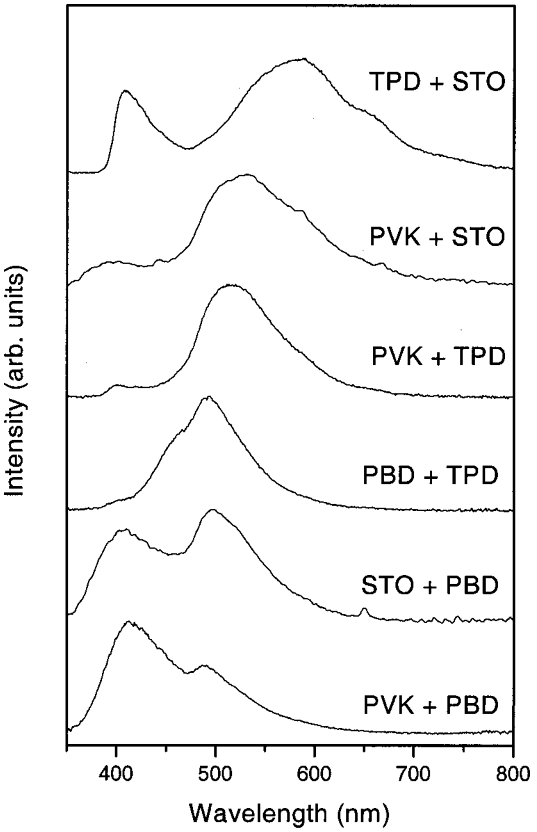

FIG. 2. Photoluminescence spectra of spin-coated films of the blends indicated are shown.

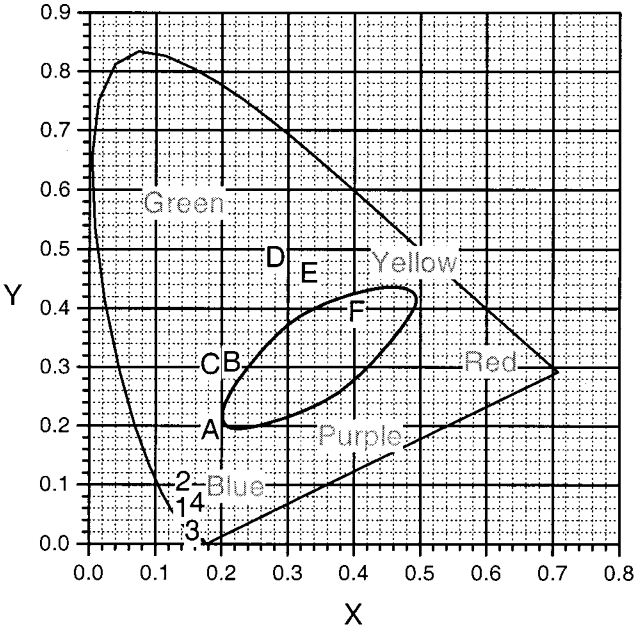

FIG. 3. CIE chromaticity diagram, with the coordinates of the spectra of Fig. 1 (1=TPD, 2=PVK, 3=PBD, and 4=STO) and Fig. 2 (A=PVK+PBD, B=STO+PBD, C=PBD+TPD, D=PVK+TPD, E=PVK+STO, and F=TPD+STO) are shown.

emissions shown in Fig. 1. The result of the broadband nature of the spectra of Fig. 2, combined with the residual blue emission, is that the emissions appear to be white—almost pure white in the case of TPD/STO, with hints of yellow, green, or blue for the other blends. To quantify these observations, chromaticity coordinates, using the Commision Internationale l'Eclairage (CIE) (1931) color matching functions, were calculated from the spectra of Figs. 1 and 2, and are plotted on the diagram of Fig. 3. The solid oval in Fig. 3 indicates the approximate area where the human eye perceives the color as white. Note that the coordinates of all the blends lie well outside the gamut of colors that can be formed by a superposition of two or more of the individual molecules.

UV/visible absorption spectroscopy of the spin-coated films indicated the absence of any new chemical species that might give rise to redshifted emission. For example, the absorption spectrum of the TPD+STO film, Fig. 4(a), shows no new features compared to the spectra of the individual components, Figs. 4(b) and 4(c). A broadband, redshifted emission spectrum, with no new chemical species formed, is characteristic of exciplex formation.[5] An exciplex is a complex formed between the excited state of a molecule and the ground state of a different molecule, as shown in Fig. 5. Excitation of the molecule with the lowest electron affinity, the donor, is followed by electron transfer to the other molecule, the acceptor. The resulting complex electron–hole pair can then decay via photon emission, considerably redshifted compared to that from either of the individual molecules. The donor molecule can be identified from the photoluminescence excitation (PLE) spectrum: for example the PLE spectrum of TPD+STO, Fig. 4(d), has the same form as the absorption spectrum of TPD, Fig. 4(c), rather than that of STO, Fig. 4(b). This is consistent with the electron affinities, 3.0 eV for STO,[6] and 2.4 eV for TPD 2.4,[7] since the donor molecule is required to have the lower electron affinity, as shown in Fig. 5. Exciplex formation is favored where there is significant spatial overlap between the lowest unoccupied molecular orbitals (LUMOs) of the constituent species,[5]

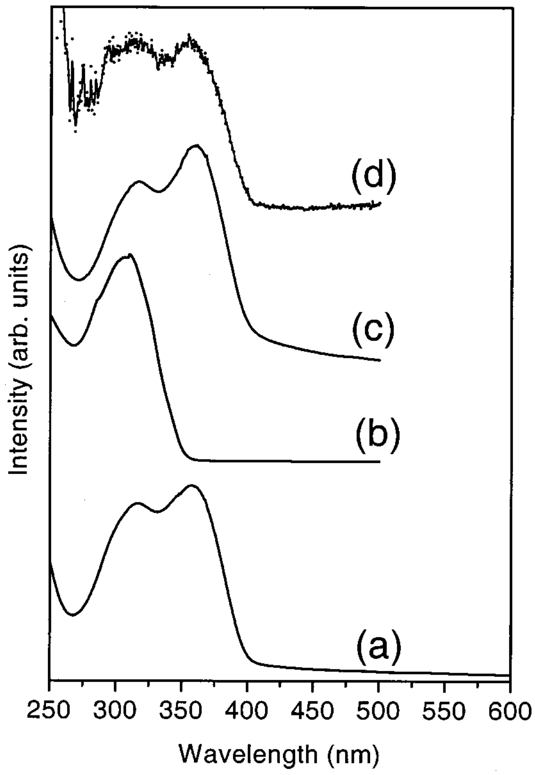

FIG. 4. Absorption spectra of (a) TPD+STO film, (b) STO, and (c) TPD are shown. PLE spectrum (d) of TPD+STO is presented.

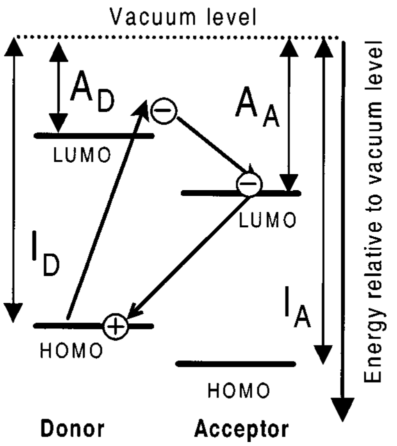

FIG. 5. Energy level diagram showing the mechanism of exciplex formation is shown. A_D, I_D and A_A, I_A are the electron affinities and ionization potentials of the donor and acceptor molecules, respectively.

which is clearly the case for conjugated organics, whose LUMOs are highly delocalized π orbitals. Exciplex formation between electroactive polymers was observed several years ago,[8,9] but they are still relatively little studied in the field of organic LEDs, although exciplex formation at the organic–organic interface has been observed in isolated cases for multilayer devices,[10–13] including at least one white emitting device.[14]

Given that all electroactive molecules have the delocalized π orbitals which favor their formation, we suggest that the occurrence of exciplexes, leading to white or near-white emission, is likely to be a general phenomenon in blended blue-emitting organics. Note that even the PVK/PBD blend, which remains dominated by the blue emission of the individual molecules, clearly shows exciplex formation. Our results show that it is not limited to polymer–polymer blends, nor to interfaces. It is likely that fine tuning of the composition of the blends could produce truer white, or colored near-whites as required. We conclude that blends of blue-emitting molecules may represent a simple, cheap, and general method to obtain white emission from organic LEDs.

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