

## Energy transfer processes among emitters dispersed in a single polymer layer for colour tuning in OLEDs

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The energy transfer processes taking place in a single polymeric layer that enable the definition of the three primary colours (red, green and blue) in selected areas via photochemically induced emission tuning are discussed. The polymers used as hosts are two wide band gap polymers, PVK and a polyfluorenyl derivative. In the polymer matrix are dispersed the green emitter, 1-(4'-dimethyl-aminophenyl)-6phenyl-1,3,5-hexatriene (DMA-DPH), the red emitter, 4dimethylamino-4'-nitrostilbene (DANS) and a photoacid generator (PAG). Upon irradiation, protons are released from the PAG and they react gradually with the two emitters, causing the blue shift of the green emitter fluorescence and the extinction of the red emitter fluorescence. Depending on the protonation extent, the relative concentrations of the emitters and the exposure dose the energy transfer processes occurring inside the matrix result in definition of different colour emitting areas. The understanding of the energy transfer processes with photoluminescence experiments is a necessary first step in order to rationalize the selection of suitable components enabling the definition of the three primary colours in OLEDs.

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**1 Introduction** The formation of multi-layer structures represents the main route followed for the manufacture of full-color displays in OLED technology [1]. This approach requires deposition and patterning of different polymeric or small organic molecule based layers one over the other, where each one is capable of emitting one of the three main colors. Alternatively, simpler routes for colour definition in emitting diodes have been presented, as for instance the photopatterning method presented by Shirai and Kido [2], where laser irradiation is used to bleach dve molecules in a poly(N-vinylcarbazole) matrix. In a different approach Müller et al. [3] were able to demonstrate R-G-B devices by sequential patterning of red, green and blue emitting polymers, immobilizing them on the substrate by photocrosslinking and removing the noncrosslinked remnants with a solvent before casting the next polymer, whereas multi-colored OLEDs were also fabricated using the thiolene photoreaction to tune the emission



properties [4]. Interesting approaches that could also be used in OLED technology have been reported in the broader field of fluorescence imaging in polymeric films for possible applications in lighting, image recording, sensing and displays [5]. Fluorescent organic dyes dispersed in the polymer film or moieties pending to the polymer itself have been also used for fluorescence imaging to monitor acid diffusion in the area of lithographic processing [6], where acid-induced changes of emission properties usually result in production of fluorescent and non-fluorescent areas (acid-induced dye quenching) [5, 6]. Recently [7] we presented the successful formation of RGB pixels in the same polymer layer by using a wide band gap conducting polymer along with two emitters and a photoacid generator. In the present paper we further discuss the energy transfer mechanisms taking place in these processes using absorbance and photoluminescence data with the aim to better understand the rules for the selection of appropriate components and improve the proposed technology. In this context two wide band gap conducting polymers, PVK and a polyfluorenyl derivative, are compared according to their ability of serving as hosts for our green-blue (DMA-DPH) and red (DANS) emitters.

## 2 Experimental

**2.1 Materials and instrumentation** Fluorescent dyes 1-(4'-dimethyl-aminophenyl)-6-phenyl-1,3,5-hexa-triene (DMA-DPH) and 4-dimethylamino-4'-nitrostilbene (DANS) were purchased from FLUKA. The photoacid generator (PAG) used was triphenylsulfonium trifluoro-methane sulfonate purchased from Midori Kagaku Co., Ltd. Poly(9-vinylcarbazole) (PVK) and the polyfluorenyl derivative poly[9,9-di(2'-ethylhexyl)fluorenyl-2,7-diyl] (PF) were purchased from Aldrich and used with no further purification.

For absorption spectra a Perkin-Elmer Lambda-16 spectrometer was employed. Fluorescence and excitation measurements were recorded with a Perkin-Elmer LS-50B fluorescence spectrometer.

**2.2 Polymeric film preparation and processing** Solutions containing PVK or PF (40 mg/ml on 1,1,2,2 tetrachloroethane) were prepared. Then, there were also added the PAG along with the red (DANS) and green (DMA-DPH) emitters in various concentrations (% weigth of polymer mass). Films were spin-coated from filtered solutions at 2000 rpm and then baked on a hotplate at 80 °C for 10 min. Photoacid generation was induced by exposing films with a 500 W Oriel Hg-Xe exposure lamp through a 248 nm narrowband filter (6.5 nm half band width) for various times. The incident power was measured with a IL 1700 International Light Radiometer and was found  $0.21 \pm 0.02 \text{ mJ} \cdot \text{s}^{-1} \text{cm}^{-2}$ .

3 Results and discussion In our recently published work [7], the photochemically induced emission tuning for the definition of the three primary colours (R-G-B) in a single conducting polymeric layer was reported. The colour tuning is based on the photochemically induced protonation of two fluorescent emitters; the initially green fluorescent emitter 1-[4-(dimethylamino)phenyl]-6-phenylhexa-1,3,5,-triene (DMA-DPH), resulting in the hypsochromic (blue) shift of the emission wavelength for its protonated form [8], and the initially red emitter 4dimethylamino-4'-nitrostilbene (DANS) [9], whose emission disappears after protonation of the amino group. The photochemically induced protonation is achieved by exposure of a photoacid generator (PAG) to ultra-violet light (248 nm, maximum absorbance wavelength), which leads to the release of a proton  $(H^+)$ . The observable shift of the DMA-DPH emission upon protonation arise from changes in charge delocalisation in the extended conjugated system of the molecules induced by the electron donating effect of the *p*-dimethylamino group in the original (unprotonated) forms. Consequently, the protonation desrupts this conjugation and results in the observed spectral changes [10] (Scheme 1). An additional quenching mechanism has been proposed for DANS, according to which the non-radiative state is characterized by a twisting of the nitro group [11].



**Scheme 1** The photoacid generator produces a proton upon ultra violet irradiation (248 nm filter). The proton reacts with the dimethylamino group of DANS resulting in the extinction of its initially red fluorescence.

In the present study we investigated the shift of absorption upon protonation. As shown in Fig. 1, the absorption band of DANS at 445 nm disappears after irradiation in the presence of a photoacid generator and a new band appears at 345 nm. On the other hand, the initial emission at 605 nm is quenched.



**Figure 1** UV-Vis Absorption spectra of film spin cast from a solution containing 4% w/w DANS and 8% w/w PAG in 4% w/w PMMA in MIBK matrix after subsequent UV irradiation at 248 nm (filter).

In this paper a more detailed view on the energy transfer mechanisms taking place in these processes is presented. This study is based on absorbance and photoluminescence experiments that can give a first insight on materials selection principles and will be further completed with electroluminescence data in a forthcoming publication. Our present system comprises a conducting polymer matrix, along with the two emitters, DMA-DPH and DANS, and the photoacid generator (PAG). The polymer used was either the wide band gap conducting polymer poly(9vinylcarbazole) (PVK) [12] or the lately introduced polyfluorenyl derivative, chosen because of its high quantum yield in solid state, poly[9,9-bis-(2-ethylhexyl)-9Hfluorene-2,7-diyl] (PF) [13].

A successful energy transfer from the PVK matrix to the fluorescent emitters and a subsequent photochemical colour tuning through successive exposure of the film to UV light (248 nm filter) was observed and will be explained below (Scheme 2). It should be noted that the main absorber at 248 nm is the photoacid generator, which on the other hand does not absorb beyond ~280 nm and, therefore, it cannot be excited by visible light.



Scheme 2 RGB colour tuning on a single polymer layer. A PVK solution containing 2% w/w DMA-DPH, 1% w/w DANS and 8% PAG was spin coated on a glass substrate and exposed at 248 nm (selected with filter) UV light through mask for different exposure times ("dose 1" corresponds to 105 mJ·cm<sup>-2</sup> and "dose 2" to 315 mJ·cm<sup>-2</sup>).

It is well known [14] that transfer of the excitation energy may occur in the case where the emission of a quantum of light by one molecule (donor,  $D^* \rightarrow D + hv$ ) is followed by absorption of the emitted photon by a second molecule (acceptor,  $A + hv \rightarrow A^{*}$ ). This mechanism requires that the excited energy donor molecule D<sup>\*</sup> emits photons, which are then absorbed by the energy acceptor molecule A. So, the rate or probability per unit time of energy transfer from D<sup>\*</sup> to produce A<sup>\*</sup> will depend on the quantum yield of emission by  $D^*$  (ideally  $\Phi^{D}_{e} \approx 1$ ), the number of A molecules (high concentration of A) in the path of photons emitted by D<sup>\*</sup>, the light absorbing ability of A (high extinction coefficient of A) and the good overlap of the emission spectrum of D<sup>\*</sup> and absorption spectrum of A (big spectral overlap integral, J). Mathematically, J is given by:

$$J \equiv \int_{0}^{\infty} I_D \varepsilon_A d\bar{\nu} \tag{1}$$

where  $I_D$  is a graph of the experimental emission of D<sup>\*</sup> and  $\varepsilon_A$  is a graph of the experimental absortion spectrum of A, both plotted on an energy scale (usually cm<sup>-1</sup>) and normalised so that complete overlap would correspond to J = 1. Further below, a qualitative study of energy transfer

through the degree of overlap between emission and absorption spectra will be presented.

In our system, as can be seen in Fig. 2, the emission spectrum of PVK (solid line 1) overlaps significantly with the absorption spectra of both DMA-DPH and DANS (dashed lines 2a and 3a respectively). Nevertheless, the ob-

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served emission for the system (solid line 3b) containing both emitters is identical to that of the red probe (DANS). This can be explained by taking into consideration two possible mechanisms: a one-step and a two-step energy transfer mechanism. This means that PVK transfers its energy either directly to DANS or initially to DMA-DPH (larger spectral overlap between 1 and 2a than 1 and 3a), which in its turn transfers the gained energy to DANS, since the DANS absorption spectrum (dashed line 3a) matches significantly the emission spectrum of DMA-DPH (solid line 2b). In both cases our initial film emits finally red light.



**Figure 2** Photoluminescence (solid lines) and absorption (dashed lines) spectra in red emitting pixels. The films were cast from (1) PVK, (2a,b) 4% w/w DMA-DPH and (3a,b) 4% w/w DANS. Both emitters were inserted in the PVK matrix along with 10% w/w PAG. All spectra are normalised to PVK for comparison.

As we expose now our film to ultra-violet light at dose 1 (105  $mJ\cdot cm^{-2}$ ), the photochemical reaction mentioned above takes place and the PAG produces protons, which in turn protonate the amino groups of the two emitters. The number of produced protons and subsequently, the degree of protonation increases with increase of the irradiation dose. Thus, after the film has been irradiated at a certain dose, and given that DANS is being dispersed at a lower concentration than DMA-DPH (1:2 molar concentration) inside the polymer matrix, the unprotonated DANS molecules will be present at a very low concentration, whereas the concentration of unprotonated DMA-DPH molecules will be higher. It should be mentioned that the two probes have comparable basicities, due in both cases to the the dimethylamino group, meaning that the photoacid generated proton has almost equal probability to protonate any of them.



**Figure 3** Photoluminescence (solid lines) and absorption (dashed lines) spectra of films in green emitting pixels. The films were cast from (1) PVK, (2a,b) 4% w/w DMA-DPH non protonated form, (2c) 4% w/w DMA-DPH protonated form and (3a,b) 4% w/w DANS protonated form. Both emitters were inserted in the PVK matrix along with 10% w/w PAG. Protonated forms obtained by exposure to UV light (248 nm filter) at an optimised dose (dose 1; 500 s or 105 mJ·cm<sup>-2</sup> at our experimental conditions). All spectra are normalised to PVK for comparison.

It was experimentally found, that when the exposure dose is optimized, such a system emits green colour, identical to the emission of DMA-DPH alone (Fig. 3, solid line 2c). The protonation of DANS results in the blue shift of the absorption spectrum (Fig. 3, dashed line 3a, see also Fig. 1), so that it does not overlap any more with the emission of PVK (solid line 1), resulting in insufficient energy transfer from PVK to the protonated form of DANS. Additionally, the emission of the protonated form of DANS (solid line 3b) is eliminated, meaning that even a small remaining spectral overlap is no more capable of giving red emission. Consequently, the matching of the absorption spectrum of the non-protonated DMA-DPH (dashed line 2a) and the PVK emission (solid line 1) gives rise to green emission (solid line 2b). It should be noted, that the absorption spectrum of the DMA-DPH non-protonated form (dashed line 2a) overlaps much better with the PVK emission than the absorption spectrum of the protonated form (dashed line 2c). In addition, blue emission from the latter should not be expected, if a substantial amount of the unprotonated form is present in the system, since effective energy transfer to the unprotonated form is taking place (see Fig. 4, solid line 2b and Fig. 3, dashed line 2a).

Finally, with further irradiation of the film (total exposure time under our experimental conditions: 1500 s, corresponding to a dose of 315 mJ·cm<sup>-2</sup>), a blue emission arises (Fig. 4, solid line 4). This emission is a combination of the emission of the fully protonated form of DMA-DPH (solid line 2b), as well as the emission of PVK itself (solid line 1). Thus, it is located in an intermediate wavelength between the two aforementioned emissions of the plain compounds.



**Figure 4** Photoluminescence (solid lines) and absorption (dashed lines) spectra of films in blue emitting pixels. The films were cast from (1) PVK, (2a,b) 4% w/w DMA-DPH protonated form and (3a,b) 4% w/w DANS protonated form. Both emitters were inserted in the PVK matrix along with 10% w/w PAG. Protonated forms obtained by exposure to UV light (248 nm filter) at an optimised dose (dose 2; 1500 s or 315 mJ·cm<sup>-2</sup> at our experimental conditions). (4) Photoluminescence spectrum of film cast from PVK with 2% w/w DMA-DPH, 1% w/w DANS and 4% w/w PAG and exposed at UV light under 248 nm filter at dose 2. All spectra are normalised to PVK for comparison.

Based on the above considerations, it becomes clear how a successful colour tuning based on the photochemical protonation of two emitters dispersed along with a PAG in a single polymer layer was achieved. This emission colour tuning depends mainly on the relative concentration of the above emitters as well as the concentration of the PAG and the irradiation dose, namely the exposure time. Nevertheless, PVK has a relatively poor quantum yield, rendering it rather unsatisfactory for OLED applications. For this reason another conducting polymer, a polyfluorenyl derivative, poly[9,9-di(2'-ethylhexyl)fluorenyl-2,7-diyl] (PF), was also tested as the polymer host. In this case, colour tuning from red to blue was not achieved. Instead of that, a wide emission spectrum was finally observed, corresponding to almost white light.

In more detail, the starting system emits green colour (Fig. 5, solid line 4), although the energy transfer from PF to DANS is theoretically successful (good matching of the PF emission spectrum (solid line 1) with the DANS absorption spectrum (dashed line 3a)). The reason for this emission is that the PF alone has a very intense blue-green emission, exhibiting three peaks at 415 nm, 440 nm and 510 nm (solid line 1). Thus, the final emission is at an intermediate wavelength (solid line 4, 525 nm), as it is due to a mixed emission from both DANS and PF.

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**Figure 5** Photoluminescence (solid lines) and absorption (dashed lines) spectra of films cast from (1) PF, (2a,b) 4% w/w DMA-DPH and (3a,b) 4% w/w DANS. Both emitters were inserted in the PF matrix along with 10% w/w PAG. (4) Photoluminexcence spectrum of film cast from PF with 2% w/w DMA-DPH, 1% w/w DANS and 4% w/w PAG. All spectra are normalised to PF for comparison.

Thereafter, the subsequent exposure of the film to ultra-violet light at dose 1 (105 mJ·cm<sup>-2</sup>) results, as explained before, in the extinction of the red fluorescence, and the observed emission comes from the non-protonated DMA-DPH (Fig. 6, solid line 4). The DMA-DPH emission at 475 nm (solid line 2b) is further enhanced by the green emission of the PF itself (solid line 1), while the peak corresponding to the blue emission at 415 nm is significantly decreased (bold solid line 4).



**Figure 6** Photoluminescence (solid lines) and absorption (dashed lines) spectra of films cast from (1) PF, (2a,b,) 4% w/w DMA-DPH, 2c) 4% w/w DMA-DPH protonated form and (3a,b) 4% w/w DANS protonated form. Both emitters were inserted in the PF matrix along with 10% w/w PAG. Protonated forms obtained by exposure to UV light (248 nm filter) at dose 2. (4) Photoluminescence spectrum of film cast from PF with 2% w/w DMA-DPH, 1% w/w DANS and 4% w/w PAG and exposed at UV light under 248 nm filter at an optimised dose (dose 1). All spectra are normalised to PF for comparison.

Finally, when DMA-DPH is fully protonated after a longer exposure (dose 2, 315 mJ·cm<sup>-2</sup>), the emission is not blue and therefore it does not correspond to the expected emission from the protonated DMA-DPH (Fig. 7, solid line 2b). A wide emission, almost white (starting from 400 nm up to 600 nm, solid line 4), is observed, coming from the mixed emission of protonated DMA-DPH (solid line 2b, 440 nm) and the PF itself (solid line 1).



**Figure 7** Photoluminescence (solid lines) and absorption (dashed lines) spectra of films cast from (1) PF, (2a,b) 4% w/w DMA-DPH protonated form and (3a,b) 4% w/w DANS protonated form. Both emitters were inserted in the PF matrix along with 10% w/w PAG. Protonated forms obtained by exposure to UV light (248 nm filter) at dose 2. (4) Photoluminescence spectrum of film cast from PF with 2% w/w DMA-DPH, 1% w/w DANS and 4% w/w PAG and exposed at UV light under 248 nm filter at dose 2. All spectra are normalised to PF for comparison.

Consequently, although the PF has a much higher quantum yield than PVK, its wide blue green emission cannot be easily quenched and therefore, a colour tuning through the mechanism described above is not possible. On the other hand this system could be of interest in white light applications.

**4 Conclusion** Full colour tuning (RGB) in a single polymeric layer was achieved, using a suitable green emitter (DMA-DPH) and a red emitter (DANS) dispersed along with a PAG in PVK, a wide band gap polymer matrix. The energy transfer mechanisms taking place during the photochemically induced transformations of the above probes were studied in detail and the observed emission spectra were justified through this mechanism. It was shown that careful study of the relative concentrations combined with a suitable exposure time (irradiation dose) allow for the control over the degree of protonation of the emitters and subsequently the control over the emission wavelength (colour). Finally, two wide band gap polymers, poly(9-vinylcarbazole) (PVK) and the polyfluorenyl derivative poly[9,9-di(2'-ethylhexyl)fluorenyl-2,7-diyl] (PF) were

compared as potential hosts. PVK, although it is known to exhibit a rather low quantum yield, allows the definition of R-G-B areas due to better spectral characteristics, whereas the PF derivative is found to be problematic as a host for our colour tuning approach, due to its broad blue-green emission.

Further study is in progress on systems with higher quantum yield and on the electron transfer processes that are also encountered in electroluminescence experiments.

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## References

- G. Gu, V. Bolovic, P. E. Burrows, S. R. Forrest, and M. E. Thompson, Appl. Phys. Lett. 68(19), 2606 (1996); G. Parthasarathy, G. Gu, and S. R. Forrest, Adv. Mater. 11, 907 (1999); X. Jiang, Z. Zhang, W. Zhao, W. Zhu, B. Zhang, and S. Xu, J. Phys. D: Appl. Phys. 33, 473 (2000); B. W. D'Andrade, M. E. Thompson, and S. R. Forrest, Adv. Mater. 14, 147 (2002).
- [2] S. Shirai and J. Kido, J. Photopolym. Sci. Technol. 14, 317 (2001).
- [3] C. D. Müller, A. Flcou, N. Reckefuss, M. Rojhan, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, and K. Meerholz, Nature 421, 829 (2003).
- [4] A. Pogantsch, S. Rentenberger, G. Langer, J. Keplinger, W. Kern, and E. Zojer, Adv. Funct. Mater. 15, 403 (2005).
- [5] J. M. Kim, T. E. Chang, J. H. Kang, K. H. Park, D. K. Hang, and K. D. Ahn, Angew. Chem., Int. Ed. **39**, 1780 (2000); J. M. Kim, T. E. Chang, J. H. Kang, D. K. Hang, and K. D. Ahn, Adv. Mater. **11**, 1499 (1999); J.-M. Kim, Macromol. Rapid Commun. **28**(11), 1191 (2007); J.-M. Kim, Adv. Funct. Mater., in press (2007); A. M. Vekselman and C. Zhang, Chem. Mater. **9**, 1942 (1997).
- [6] B. Lu, J. W. Taylor, F. Cerrina, C. P. Soo, and A. J. Boordillion, J. Vac. Sci. Technol. B 17(6), 33450 (1999); P. L. Zhang, S. Webber, J. Mendelhall, J. Byers, and K. Chao, Proc. SPIE 3333, 794 (1998); U. Okoroanyanwu, J. D. Byers, T. Cao, S. E. Webber, and C. G. Wilson, Proc. SPIE 3333, 747 (1998).
- [7] M. Vasilopoulou, D. Georgiadou, G. Pistolis, and P. Argitis, Adv. Funct. Mater. **17**, 3477 (2007).
- [8] G. Pistolis, S. Boyatzis, M. Chatzichristidi, and P. Argitis, Chem. Mater. 14, 790 (2002).
- [9] C. Splitter, J. Org. Chem. 20, 1086 (1955).
- [10] G. Pistolis and A. Malliaris, Langmuir, 13, 1457 (1997).
- [11] A. M. Moran, G. P. Bartholomew, G. C. Bazan, and A. M. Kelley, J. Phys. Chem. A **106**, 4928 (2002).
- [12] J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, Appl. Phys. Lett. 63, 2627 (1993).
- [13] M. Gross, D. C. Müller, H. G. Nothofer, U. Scherf, D. Neher, C. Bräuchle, and K. Meerholz, Nature, 405, 661 (2000).
- [14] N. J. Turro, Modern Molecular Photochemistry (University Science Books, Sausalito, California, 1991), p. 298.

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