Exciton dynamics in blends of phosphorescent emitters

Christoph Schütz[1], Bianca Höfer[1, 2], Frank Jaiser[1], Hartmut Krueger[3], Manuel Thesen[3], Silvia Janietz[3], and Anna Köhler[*, 1, 2]

[1] Institute of Physics, University of Potsdam; 14469 Potsdam, Germany
[2] Institute of Physics, University of Bayreuth; 95440 Bayreuth, Germany
[3] Fraunhofer Institute of Applied Polymer Research; 14476 Potsdam, Germany

[*] Corresponding author: e-mail Anna.Koehler@uni-bayreuth.de, Phone: +00 49 921 55 2600

Cascading energy transfer is a usually undesired effect in organic-host guest systems that are designed for light-emitting purposes. Here we demonstrate a chemical approach to suppressing undesired energy transfer from the blue to the red emitter in multicomponent polymer blends. We have combined a red, green and blue emitting Ir-complex each with charge transporting molecules to a side-chain copolymer. The covalent attachment of the phosphorescent emitter is found to prevent cascading energy transfer through steric shielding. This approach approximately doubles the efficiency and brightness of polymer light emitting diodes.

1 Introduction Organic light-emitting diodes (OLEDs) have by now demonstrated efficiencies and brightness that enable applications not only for display functions but also for lighting purposes [1–3]. High luminescence yields can be achieved through the use of host-guest systems comprising charge-transporting molecules and phosphorescent emitters such as Iridium complexes [4–7]. The white colour of the emission that is needed for lighting purposes can be obtained by blending blue, green and red emitters in suitable ratios in the charge transporting matrix [8]. This concept suffers from two drawbacks. First, phase separation between the different blend components is a frequent problem. Second, cascading energy transfer from the blue emitter to the green and red emitters implies that comparatively high proportions of blue and green emitter are needed to obtain white emission and that furthermore the emission colour is very sensitive to compositional variations.

Here we present a novel synthetic approach to prevent phase separation and, more importantly, to reduce this undesired energy transfer. We covalently attach a blue, green or red emitter each with an electron transporting moiety and a hole transporting moiety to a polystyrene backbone in order to form a side-chain terpolymer. The resulting three terpolymers are then mixed together (combination system A) (Fig. 1). We observe that cascading energy transfer is reduced both in electroluminescence and photoluminescence in the terpolymer blend compared to a mixture of the corresponding charge transporting copolymer with the individual functionalized triplet emitters (combination system B).

2 Experimental The hole-transporting di-p-tolyl-(4-vinyl-phenyl)-amine was synthesized in a yield of 86% by a Wittig-reaction from N,N-bis-(4-methylphenyl)-amino-benzaldehyde obtained from Sensient Imaging Technologies GmbH. The electron-transporting 2-(4′-tert-butyl-biphenyl-4-yl)-5-(4-vinyl-phenyl)-[1,3,4]-oxadiazole was synthesized in an overall yield of 40% by a three step reaction starting from 2-(4′-tert-butyl-biphenyl-4-yl)-5-phenyl-[1,3,4]-oxadiazole obtained from Sigma-Aldrich. As polymerizable saturation ligand for the different phosphorescent emitters 6-(4-vinyl-phenyl)-hexane-2,4-dione was chosen which was synthesized from acetylacetonate and chloromethylstyrene. The polymerizable phosphorescent Ir-complexes were synthesized form the $[\{Ir(L1)_2Cl\}_2]$-complexes with 6-(4-vinyl-phenyl)-hexane-2,4-dione (L1 is 2-phenylpyridine for green, 2-(2,4-difluorphenyl)-pyridine

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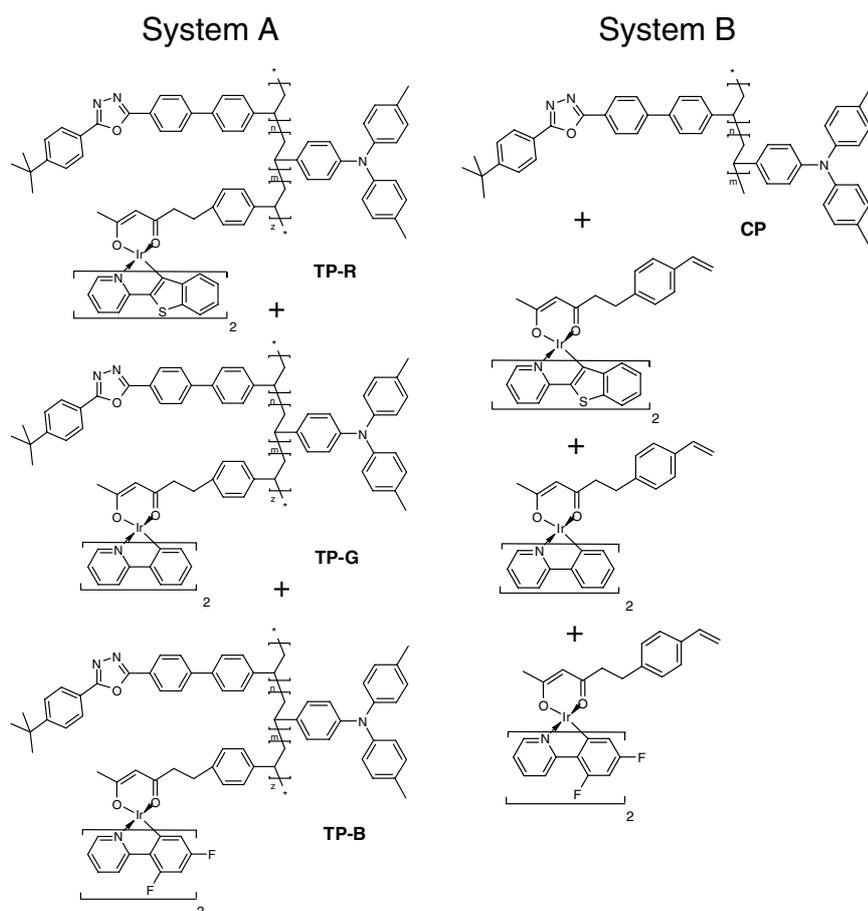
Figure 1 Chemical structure of the materials and the material systems used. *n*, *m*, *z* denote the molar ratios of the components (see Table 1).

for blue and 2-benzo[b]thiophene-2-yl-pyridine for red emission). The polymers were obtained by standard radical polymerisation of the monomer mixture in tetrahydrofurane with 2,2-azobis(2-methylpropionitrile) as initiator. The chemical structure and purity of the monomers were checked by elemental and NMR analysis, the glass transition by DSC. The copolymer composition was determined by NMR analysis. The molecular weights were identified by gel permeation chromatography. The results are summarized in Table 1.

For photoluminescence measurements, about 100 nm thick films were spun from Chloroform solutions (concentrations 10 g/l to 15 g/l, spinning speed 1200 rpm) onto quartz substrates. During the measurements, the samples

were held in a continuous flow Helium cryostat and were meas-ured under vacuum (for 300 K measurements) or in a small background pressure of Helium (for 4 K measurements). Excitation was provided by the frequency tripled output of a Nd:YAG laser at 355 nm pulsed at 10 Hz with a pulse duration of about 10 ns. The emission was detected with either a CCD camera Andor iDus coupled to a Oriel spectrograph MSH201 for steady state emission or a gated intensified ICCD camera Andor iStar coupled to a Oriel spectrograph MS257.

For electroluminescence measurements, light-emitting diodes (LEDs) were fabricated. Glass substrates with a transparent, pre-patterned Indium-tin oxide (ITO) electrode (thickness 125 nm, resistivity <20 Ohm/square) were cleaned by ultrasonication in acetone, detergent solution, clean water and isopropanole. The substrates were oxygen plasma treated and a 20 nm thin layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDT:PSS) obtained from H.C. Starck was spin coated on top and baked at 200 °C for 30 minutes. The PEDT:PSS layer was about 20 nm as measured with a DEKTAT 3ST surface profilometer. The active layer of combination system A or B was spin coated at a thickness of about 100 nm from the same solution as for photolumi-nescence measurements. The films were dried at 60 °C for

Table 1 Properties of the co- and terpolymers.

poly-mer	oxadia-zole (% per mole)	triphenyl-amine (% per mole)	emitter (% per mole)	M_n (10^3 g/mole)	M_w (10^3 g/mole)	T_g (°C)
CP	71.0	29.0	–	19.0	52.1	191
TP-R	67.0	30.7	2.3	33.9	74.7	196
TP-G	66.0	31.7	2.3	22.3	61.3	194
TP-B	66.8	31.1	2.1	28.2	67.8	197

30 minutes. Finally, the cathode of 20 nm Calcium and 100 nm Aluminum was thermally evaporated. Film thicknesses were not further optimized for the material system investigated here. Each substrate held 6 single pixels. The device area defined by the overlap of ITO and Ca electrodes was 0.16 cm^2. Device characterisation was done in a nitrogen atmosphere glove box using a Keithley 2400 SourceMeter as voltage source and a Ocean Optics HR2000 CCD spectrometer.

3 Results and discussion Figure 2 displays the thin film photoluminescence spectra (PL) at 300 K of the three (separate) terpolymers as well as a comparison of the composites system A and B. The spectral emission from the in-
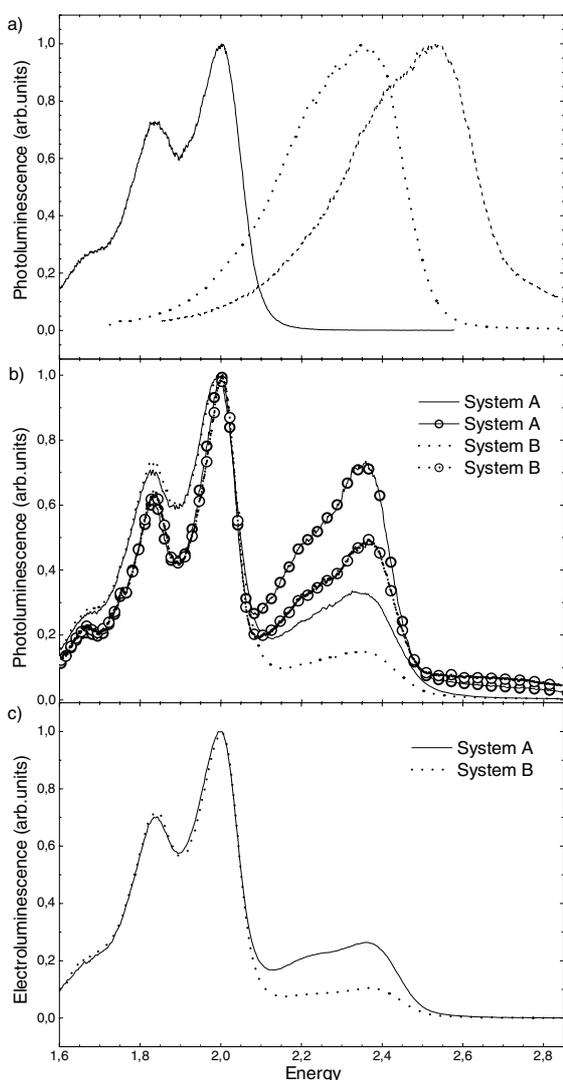

Figure 2 Photoluminescence spectra of (a) the blue (dashed line), green (dotted line) and red (solid line) emitting terpolymers at 300 K and of (b) systems A (solid line) and B (dotted line) at 300 K. The emission at 4 K is also shown (solid or dotted line with circles). (c) The 300 K electroluminescence spectra of the systems A (solid line) and B (dotted line).

dividual terpolymers agrees with that of the analogous non-functionalised Iridium complexes [9–11]. The emitters show the vibrational 0–0 peak at 2.00 eV, 2.35 eV and 2.53 eV and are referred to as red, green and blue for simplicity, though the nominally "blue" emission is of a turquoise shade. In the composite systems, equal ratios of blue, green and red emitter are used, yet in both systems, the red emission is dominant while the blue emission is barely visible. This is well-known as cascading energy transfer. When normalizing the emission spectra to the peak of the red emission band, we note a higher intensity of the green emission centred around 2.35 eV in system A compared to system B. This points to a reduced energy transfer in the terpolymer blend. The energy transfer is partially temperature activated as is evident from the higher ratio of the green to the red band emission at 4K. Even at this low temperature, energy transfer from green to red is suppressed in system A.

In order to investigate this possible reduction in energy transfer, the decay of the PL in the blend has been monitored in the blue, green and red spectral range. The blue emitter decays with a higher rate then the green emitter, while the decay of the red emitter is fairly slow (see Fig. 3). This is expected as energy transfer adds to the intrinsic decay rate of the blue or green emitter and so reduces the photoluminescence lifetime. We find that in system A, the lifetimes of the blue and green terpolymer are longer than in system B and we attribute this to a reduced energy transfer rate.

This reduced energy transfer also manifests itself in the electroluminescence properties of the compounds. Analogous to optical excitation, the green emission band also takes a higher relative intensity for electrical excitation (Fig. 2 (c)). The blue emission band, already very weak for optical excitation, is not visible for electrical excitation, possibly due to insufficient exciton formation via charge trapping on the blue dopand. The electroluminescence efficiencies of LEDs made of system A and system B are compared in Table 2 for devices operated at 12 V. System
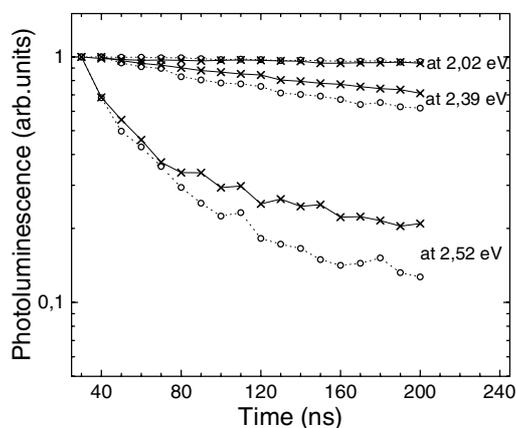

Figure 3 Decay of the photoluminescence in the combination system A (crosses, solid line) and B (open circles, dotted line) at the emission energies corresponding to the peak of the blue (2.5 eV), green (2.4 eV) or red (2.0 eV) emission.

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Table 2 Electroluminescence efficiencies of the combination systems A and B at 12 V.

system	luminous efficiency (cd/A)	power efficiency (lm/W)	maximum brightness (cd/m²)	external quantum efficiency (%)
A	3.5	0.95	18.3	2.6
B	2.0	0.52	5.8	1.8

A, which has the reduced cascading energy transfer, gives LEDs with almost two times higher efficiencies and a three times higher brightness.

To summarise the experimental results, we observe a reduction of the energy transfer rate between blue, green and red triplet emitters. This energy transfer may occur via Förster transfer from the singlet state or Dexter transfer from the triplet state. Dexter transfer requires spatial overlap of wavefunctions and is thus strongly distance dependent. We have demonstrated that in order to decrease the energy transfer it is sufficient to reduce the steric mobility of the emitting unit by covalent attachment to the polystyrene backbone. Geometric orientation is a factor influencing the Förster transfer rate. However, in this case, the sidechains would have enough flexibility to give a dipole orientation suitable for Förster transfer. It is therefore more likely that the spatial wavefunction overlap necessary for Dexter transfer cannot be obtained in the covalent attached form. We thus speculate that the covalent attachment of the emitter to the charge transporting units as a sidechain polymer suppresses Dexter-type energy transfer [12]. The luminescence spectra and electroluminescence efficiencies demonstrate clearly that this chemical approach is suitable to provide an effective route to efficient white-light LEDs. Of course, for application purposes, the choice and fractional composition of emitters still needs to be optimized.

References

[1] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, J. Appl. Phys. **90**, 5048 (2001).
[2] B. W. D'Andrade and S. R. Forrest, J. Appl. Phys. **94**, 3101 (2003).
[3] C. H. Chuen and Y. T. Tao, Appl. Phys. Lett. **81**, 4499 (2002).
[4] J. Kido, K. Nagai, and Y. Ohashi, Chem. Lett., 657 (1990).
[5] M. A. Baldo, D. F. O'Brien, Y. You, S. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature **395**, 151 (1998).
[6] V. Cleave, G. Yahioglu, P. Le Barny, D.-H. Hwang, A. B. Holmes, R. G. Friend, and N. Tessler, Adv. Mater. **13**, 44 (2001).
[7] P. A. Lane, L. C. Palilis, D. F. O'Brien, C. Giebeler, A. J. Cadby, D. G. Lidzey, A. J. Campbell, W. Blau, and D. D. C. Bradley, Phys. Rev. B **63**, 235206 (2001).
[8] J. Kido, H. Shionoya, and K. Nagai, Appl. Phys. Lett. **67**, 2281 (1995).
[9] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, and M. E. Thompson, Inorg. Chem. **40**, 1704 (2001).
[10] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, J. Am. Chem. Soc. **123**, 4304 (2001).
[11] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **79**, 2082 (2001).
[12] M. Sudhakar, P. I. Djurovich, T. E. Hogen-Esch, and M. E. Thompson, J. Am. Chem. Soc. **125**, 7797 (2003).