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The harmful influence of triplet excitons on the lifetime of polymer light-emitting diodes

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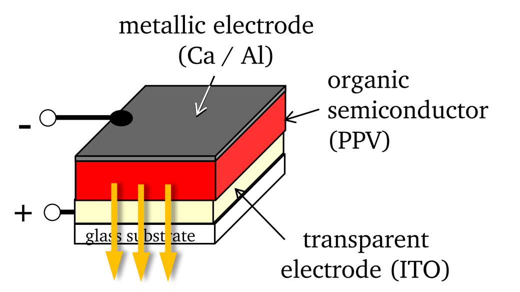
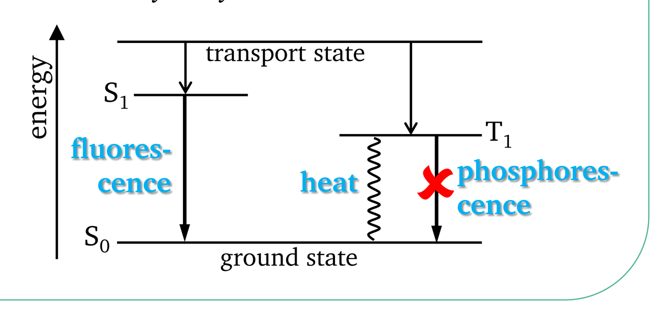
Project D4

Motivation

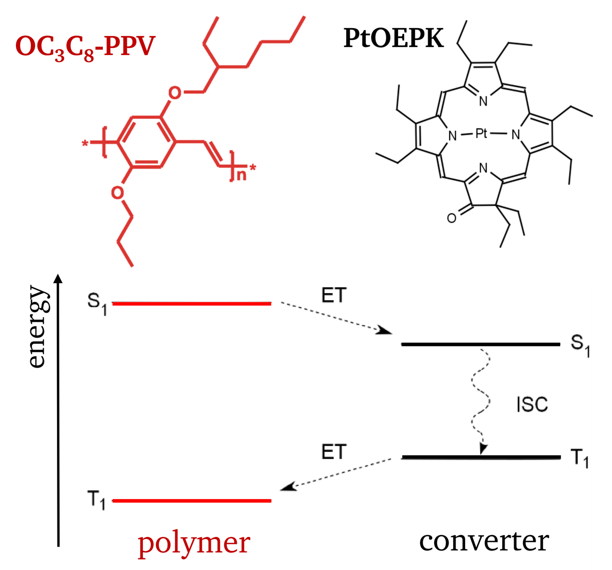
Even though organic light-emitting diodes (OLEDs) have been successfully introduced in commercial products one of the issues that is still not completely understood is the electric operation-induced degradation that will be referred to as *fatigue*.
Our studies investigate single-layer fluorescent OLEDs based on derivatives of poly(*p*-phenylene vinylene) (PPV). A lifetime-related factor investigated to a lesser extent until now is the influence of the high density of non-emissive triplet excitons (~75 %) in these devices which could be responsible for local heating or act as traps for charge carriers, leading to a degradation of the device.



The fate of excitons in an OLED

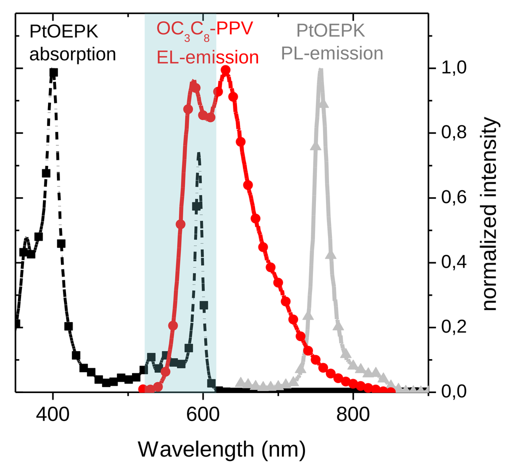


Singlet-to-Triplet Conversion in PPV

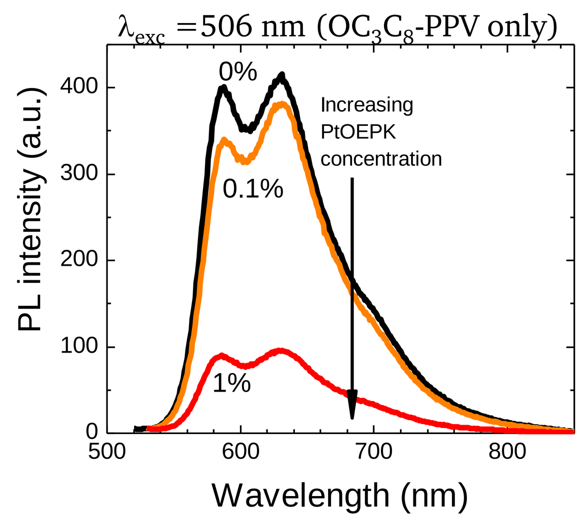


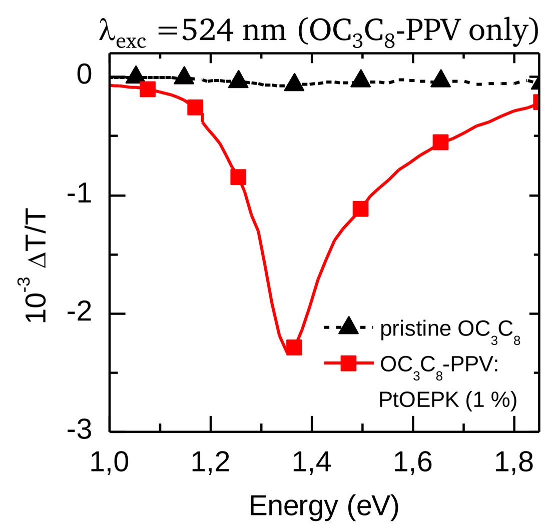
Singlet-to-triplet conversion principle

Singlet-to-triplet (S-T) conversion by blending PPV matrix with small amounts (≤1 wt%) of an appropriate sensitizer molecule. For an increase of the PPV triplet density a higher energy of the first excited singlet state of the sensitizer than that of the polymer is required and the PPV emission needs to overlap with the sensitizer absorption.



✓ Proof of S-T-conversion in sensitized layers

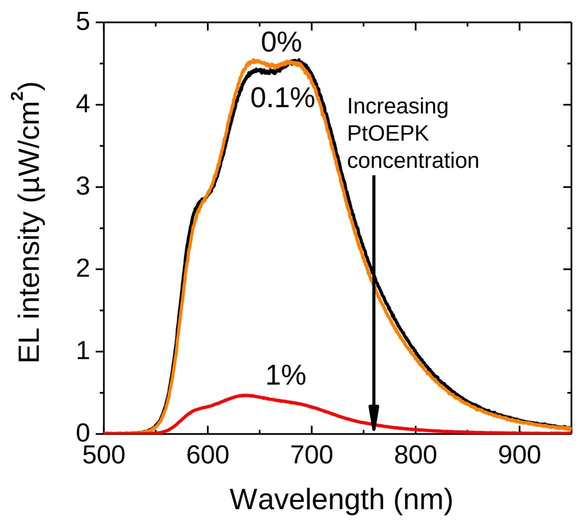


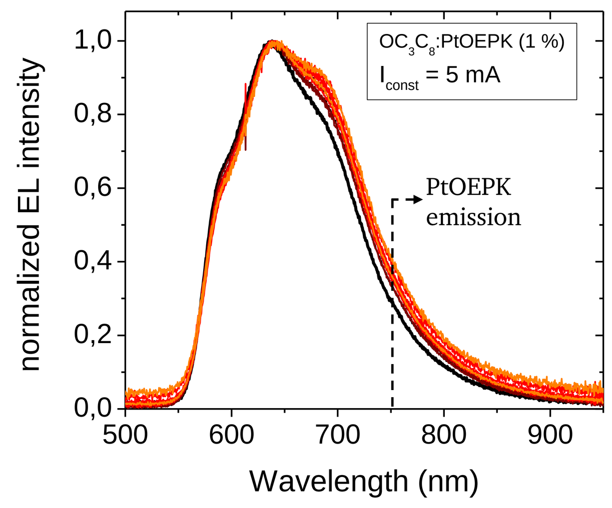


➲ The successful S-T-conversion was monitored by a decreased photoluminescence (PL) intensity of sensitized layers.

➲ Photo-induced absorption (PIA) spectroscopy probes $T_1 \rightarrow T_n$ transitions and delivers a direct proof for an increased triplet density in sensitized layers.

✓ Proof of S-T-conversion in sensitized OLEDs





➲ The successful S-T-conversion was monitored by a decreased electroluminescence (EL) intensity of sensitized devices, respectively.

➲ Electroluminescence emission spectrum does not change during fatigue. In particular, no sign of PtOEPK phosphorescence is observed at 750 nm.

Conclusion

The conversion of OC_3C_8-PPV singlet excitons to triplets by the addition of the sensitizer molecule PtOEPK could be successfully proven in layers and devices. Even though the charge carrier mobility remains rather unaffected, the increased triplet density has been found to drastically shorten the lifetime of sensitized OLEDs. The reasons for this effect seem to be manifold and cannot be assigned to a single process.

Publications last funding period

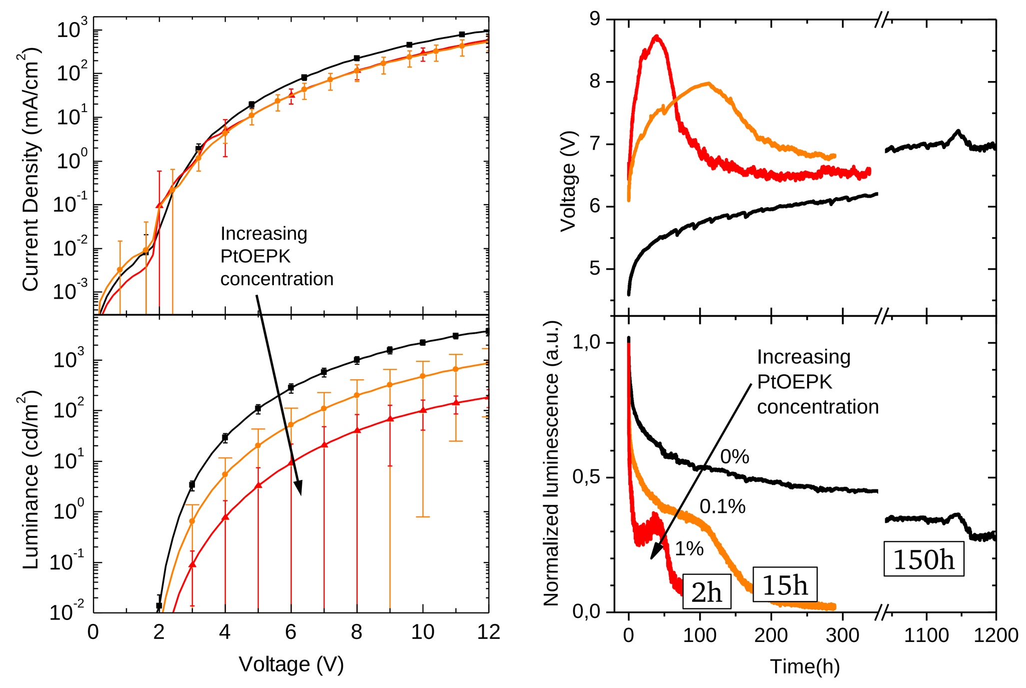
1) Y. A. Genenko, S. V. Yampolskii, C. Melzer, K. Stegmaier, H. von Seggern, "Charge carrier injection into insulating media: Single-particle versus mean-field approach", *Phys. Rev. B* **81**, 125310 (2010).

2) S. V. Yampolskii, Y. A. Genenko, C. Melzer, H. von Seggern, "Self-consistent model of unipolar transport in organic semiconductor diodes: Accounting for a realistic density-of-states distribution", *J. Appl. Phys.* **109**, 073722 (2011).

3) E. Sapper, A. Gassmann, L. Gjødvad, W. Jo, T. Granzow, J. Rödel, "Cycling stability of lead-free BNT-8BT and BNT-6BT-3KNN multilayer actuators and bulk ceramics", *J. Eur. Ceram. Soc.* **34**, 653-661 (2014).

4) O. Pekkola, A. Gassmann, F. Etzold, F. Laquai, H. von Seggern, "Influence of triplet excitons on the lifetime of polymer-based organic light-emitting diodes", *Phys. Status Solidi A*, 1 – 5 (2014) / DOI 10.1002/pssa.201330411.

Impact of an increased triplet exciton density on OLEDs



I-V-L characteristics and lifetime

➲ Current density rather unaffected in sensitized OLEDs, luminance decrease as expected due to loss of emissive singlet excitons.

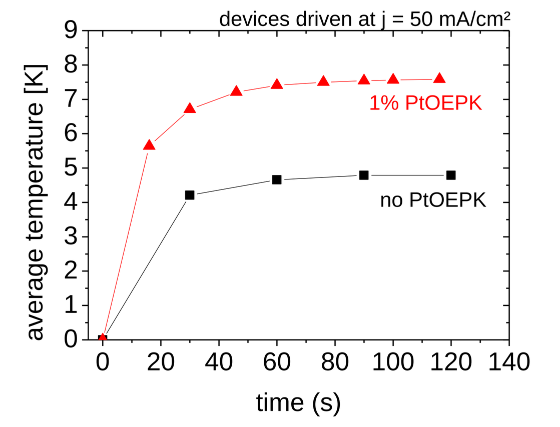
➲ Lifetime of sensitized devices drastically shortened!

PtOEPK content (wt%)	t_{50} lifetime (h)
0	150
0.1	15
1	2

Hypothesis 1: Boosted heat dissipation due to non-radiative triplet decay

As phosphorescence is spin-forbidden in PPVs, non-emissive triplet decay might be enhanced in sensitized devices leading to local heating and hot spots speeding up fatigue.

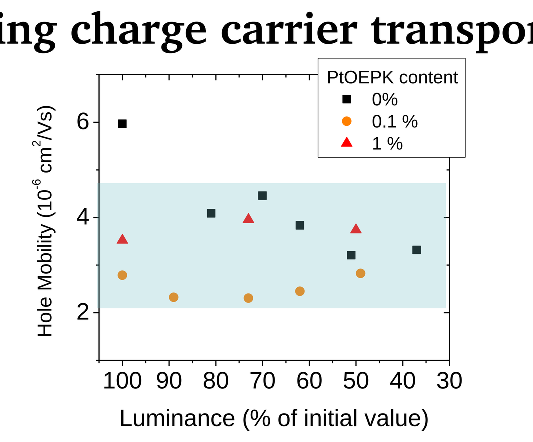
➲ Overall temperature increase too low to be solely responsible for accelerated fatigue.



Hypothesis 2: Introduction of trap states impeding charge carrier transport

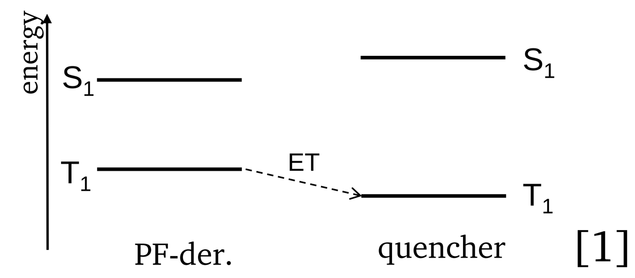
The presence of PtOEPK might influence charge carrier transport, especially for fatigued devices.

➲ Hole mobility rather invariant to the admixture of the sensitizer PtOEPK, also in the fatigued state.



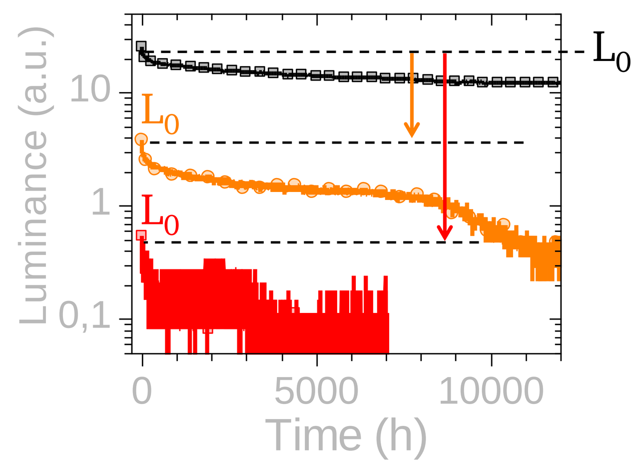
Hypothesis 3: Steepened initial decay and decreased lifetime due to contribution of triplet-triplet annihilation

According to [1] a decreased triplet density removes only the initial decay in the fatigue curves due to triplet-triplet annihilation and enlarges the lifetime.



➲ Agreement with [1] but different mechanism! In the present system the increased triplet density affects the whole fatigue curve (initial decay and plateau region).

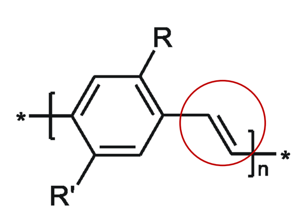
➲ Initial luminance already strongly decreased, contribution of extra singlets generated via triplet-triplet annihilation seems to be low.



[1] S. M. King, M. Cass, M. Pintani, C. Coward, F. B. Dias, A. P. Monkman, M. Roberts, J. Am. Chem. Soc. **109**, 074502 (2011).

Hypothesis 4: PPV triplet undergoes energy transfer to oxygen triplet yielding singlet oxygen attacking the PPV chain [2,3]

Destruction of polymer chain due to attack of vinylene bond. Literature reports the effect also for devices driven in the glove box [4] in nitrogen atmosphere.



➲ Such a process is thus likely to contribute to the accelerated degradation of the sensitized OLEDs.

[2] R. D. Scurlock, B. Wang, P. R. Ogilby, J. R. Sheats, and R. L. Clough, J. Am. Chem. Soc. **117**, 10194 (1995). [3] B. H. Cumpston, I. D. Parker, and K. F. Jensen, J. Appl. Phys. **81**, 3716 (1997). [4] H. Y. Low, Thin Solid Films **413**, 160 (2002).

5 Key Publications (2003-2014)

1) A. Fleissner, K. Stegmaier, C. Melzer, H. von Seggern, T. Schwalm, M. Rehahn, "Residual halide groups in Gilch-polymerized Poly(p-phenylene-vinylene) and their impact on performance and lifetime of organic light-emitting diodes", *Chem. Mater.* **21**, 4288-98 (2009).

2) K. Stegmaier, A. Fleissner, H. Janning, S. Yampolskii, C. Melzer, H. von Seggern, "Influence of electrical fatigue on hole transport in poly(p-phenylenevinylene)-based organic light-emitting diodes", *J. Appl. Phys.* **110**, 034507 (2011).

3) Y. A. Genenko, S. V. Yampolskii, C. Melzer, K. Stegmaier, H. von Seggern, "Charge carrier injection into insulating media: Single-particle versus mean-field approach", *Phys. Rev. B* **81**, 125310 (2010).

4) F. Neumann, Y. A. Genenko, C. Melzer, H. von Seggern, "Self-consistent theory of unipolar charge-carrier injection in metal / insulator / metal systems", *J. Appl. Phys.* **100**, 084511 (2006).

5) O. Pekkola, A. Gassmann, F. Etzold, F. Laquai, H. von Seggern, "Influence of triplet excitons on the lifetime of polymer-based organic light-emitting diodes", *Phys. Status Solidi A*, 1 – 5 (2014) / DOI 10.1002/pssa.201330411.