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Deep blue polymer light emitting diodes based on easy to synthesize, non-aggregating polypyrene

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Abstract: Thorough analyses of the photo- and devicephysics of poly-7-*tert*-butyl-1,3-pyrenylene (PPyr) by the means of absorption and photoluminescence emission, time resolved photoluminescence and photoinduced absorption spectroscopy as well as organic light emitting devices (OLEDs) are presented in this contribution. Thereby we find that this novel class of polymers shows deep blue light emission as required for OLEDs and does not exhibit excimer or aggregate emission when processed from solvents with low polarity. Moreover the decay dynamics of the compound is found to be comparable to that of well blue emitting conjugated polymers such as polyfluorene. OLEDs built in an improved device assembly show stable bright blue emission for the PPyr homopolymer and further a considerable efficiency enhancement can be demonstrated using a triphenylamine(TPA)/pyrene copolymer.

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1. Introduction

The cornerstones for the application of organic semiconductors were already laid in the 1960s with the discovery of organic electroluminescence [1] followed 1977 by the discovery of highly conducting doped polyacetylene [2]. Only three years after the report on the first thin film organic light emitting device (OLED) based on small molecules [3] the first polymer light emitting diode (PLED) [4] was described, triggering enormous effort within industrial and academic research. Since then light emitting small molecules as well as light emitting conjugated polymers have attracted increasing attention because of their potential as active materials for flat-panel displays [5,6] and lighting applications [7–9]. While intense research has led to well established active emitters for the red and green spectral region [10] there is still a quest for stable, highly efficient and easy to synthesize molecules emitting light in the deep blue wavelength range.

Among possible compounds for blue light emitting chromophores, pyrene is one of the most thoroughly investigated candidates. In particular pyrene is known for high fluorescence lifetime [11,12] but also its liability to form light emitting excimers (as a result of π-π-stacking of the planar molecule) shifting the blue molecular emission into the green spectral region [12,13]. While the formation of excimers made pyrene one of the most frequently applied dyes in fluorescence-labeled polymers it constitutes a limiting factor for the applicability of pyrene as blue emitter in OLEDs since excimer formation causes a significant red-shift of the fluorescence spectrum. Moreover the extraordinary long lifetime of the excited state leads to enhanced luminescence quenching thus resulting in a low solid state fluorescence quantum yield. Nevertheless, the π-π-stacking can be prevented in films by the introduction of spatially demanding substituents [14,15] or directly through avoiding the pyrene interaction via the implementation of a highly twisted structure in a pyrene polymeric chain [16]. In particular we have been able to show that in a pyrene-based polymer comprising 1,3-coupled pyrene-molecules bearing a *tert*-butyl group at the 7-position the π-π-stacking can be fully prevented. Furthermore this polymer features high solid state fluorescence quantum yield and exhibits an emission in the blue spectral region. In addition to the advantageous physical properties the polymer is highly soluble in common organic solvents and its simple 3-step synthetic route allows for a large scale synthesis of highly pure and defect-free polymers.

Following this first report on the synthesis and basic properties of poly-7-*tert*-butyl-1,3-pyrenylene (PPyr) in this contribution we report in detail on the photo-physical, electronic and device relevant properties including results on optimized devices using a triphenylamine(TPA)/pyrene copolymer. In particular absorption (UV-Vis) and photoluminescence (PL) measurements are used to investigate the observed influence of solvent polarity on the emission in solutions and in thin films. Singlet exciton (SE) and triplet exciton (TE) lifetimes were measured by means of time resolved photoluminescence (TRPL) spectroscopy and photoinduced absorption (PIA), respectively, in order to evaluate possible TE quenching effects in devices [17]. Photoemission spectroscopy (UPS) was conducted to determine the energy levels of PPyr that are relevant for the fabrication of device assemblies leading to higher luminance values, device efficiency and deep blue electroluminescence.

2. Experimental

Poly-7-*tert*-butyl-1,3-pyrenylene (PPyr) was synthesized as reported elsewhere [16]. Poly(pyrene-*co*-TPA) (PPyr/TPA) was synthesized by a Yamamoto coupling with Ni(0) from 1,3-dibromo-7-*tert*-butylpyrene and commercially available 4-bromo-N-(4-bromophenyl)-N-phenylaniline. The 1,3-dibromo-7-*tert*-butylpyrene was prepared in three steps as described for the homo-polymer in [16]. The dibromotriphenylamine was purified by three-time crystallization from *n*-hexane. The polymerization reaction was carried out with three percent of triphenylamine derivative, thus the sequence of the monomers is statistically distributed over the polymerstrand. Copolymer PPyr/TPA was precipitated in a mixture of hydrochloric acid (2 M) and methanol (1:1). After Soxhlet extraction the yield was 45% with a weight-

average molecular weight of $M_w = 27400$ g/mol as determined by GPC and a polydispersity of PD = 2.6.

For UV-Vis and PL-measurements PPyr was dissolved in toluene (TOL), cyclohexane (CH) and acetonitrile (ACN) with a concentration of 1 mg/ml. PPyr/TPA was dissolved in TOL with a concentration of 1 mg/ml. For PL-measurements thin films were spin coated on quartz-glass substrates from these solutions. Subsequently the substrates were heated at 80°C for at least one hour for solvent evaporation. Optical absorption measurements were carried out using a PERKIN-ELMER Lambda 900 spectrometer and photoluminescence (PL) spectra were taken with a Shimadzu RF5301 spectrofluorometer in air. All PL spectra were corrected with corresponding response curves of the instruments.

For TRPL measurements a solution of PPyr in toluene was prepared under inert conditions. For optical measurements thin films were spin cast from a ~1 mg/ml solution, while a concentration of ~1×10^{-3} mg/ml was used for measurements in solution. The optical investigations were performed exciting the samples with the second harmonic of a mode locked Ti:sapphire laser (380 nm), delivering 150 fs pulses with a repetition rate of 76 MHz. The repetition rate was varied by means of an optical pulse selector. PL spectra and dynamics were recorded by a Si-CCD camera and a streak camera, respectively. The Hamamatsu streak camera was used in single sweep and in synchroscan mode. All measurements were carried out at room temperature.

For PIA measurements samples were prepared by spincoating on Infrasil substrates from a toluene solution of the polymer. The pump beam was produced by an Argon-ion laser with a laser power of approximately 100 mW, mechanically chopped to provide the reference for the lock-in amplifier. The sample was mounted in an optically accessible cryostat under a dynamic vacuum of less than 10^{-5} mbar. A 50 W tungsten halogen lamp was used as the light source for the transmission measurements. All PIA spectra were measured at 100 K and were corrected for PL and the optical throughput of the setup.

For UPS studies polymers were spin coated from toluene solution on the conductive polymer (on indium tin oxide; ITO) poly(3,4-ethylenedioxythiophene)–polystyrenesulfonic acid (Baytron P VPAI 4083) (PEDOT:PSS) from H. C. Starck. UPS measurements were performed at the endstation SurICat (beamline PM4) of the synchrotron light source BESSY II (Berlin, Germany). 1,3,5-tris(1-phenyl-1H-2-benzimidazol) (TPBi) was evaporated incrementally *in situ* from a resistively heated crucible; the deposited mass-thickness was monitored with a quartz-crystal microbalance. Spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) using an excitation photon energy of 30 eV. The energy resolution was 0.1 eV. Secondary electron cutoff (SECO) spectra (used to determine the sample work function) were measured with the sample biased at −10 V to clear the analyzer work function. Standard procedures to ascertain the absence of sample charging were applied for every sample; these include variation of excitation photon flux and sample illumination with visible light. The error of reported binding energy is estimated to be smaller than +/− 0.05 eV.

Device fabrication and EL-measurements: OLEDs were assembled in a standard sandwich geometry: ITO/PEDOT:PSS/Polymer/TPBi/Ca/Al. Therefore the ITO-covered glass substrates were at first cleaned mechanically using acetone and isopropanol. Afterwards the substrates were subdued to various supersonic treatments in deionized water containing dish liquid, deionized water, toluene, and isopropanol. Finally, the cleaning procedure was finished by a dry cleaning step in oxygen plasma. A layer of PEDOT:PSS was spin-cast on the ITO electrode under ambient conditions and dried according to the specifications under dynamic vacuum. PPyr- and PPyr/TPA-layers were spin-coated from 3 mg/ml toluene solutions under argon atmosphere and dried at 80°C for 2 h in vacuum resulting in layer thicknesses of 55 nm for PPyr and 60 nm for PPyr/TPA films. The cathode materials were thermally evaporated in an evaporation chamber with an initial base pressure $<1.0 \times 10^{-6}$ mbar.

At first as an electron transport layer 10 nm of TPBi were deposited onto the whole substrate. Afterwards Ca (10nm) and Al (100 nm) were evaporated through a shadow mask

forming a device-area of 9 mm^2. Electroluminescence (EL) spectra were acquired using an ORIEL spectrometer with an attached calibrated charge-coupled device (CCD) camera. The current/luminance/voltage (I–L–V) characteristics were recorded in a customized setup using a Keithley 2612A source measure unit for recording the I–V characteristics while recording the luminance with a Keithley 6485 Picoammeter using a calibrated photodiode. For PPyr and PPyr/TPA, respectively, a series of 18 devices was investigated. Device efficiencies exhibited a mean variation of less than 15%.
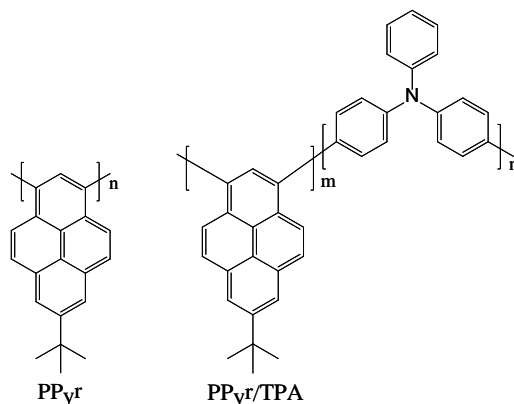

Fig. 1. left: Chemical structure of Polypyrene (n = 115), right: Chemical structure of Pyrene-Triphenylamine-Copolymer (m:n ratio is 97:3)

3. Results and discussion

The chemical structure of PPyr is depicted in Fig. 1. Absorption and PL emission spectra of PPyr in solution and in thin films were recorded and are shown normalized in Fig. 2. The spectra exhibit an absorption peak maximum for the π-π* transition of PPyr around 360 nm in solutions and within the error of measurement in thin film as well. The PL emission in a TOL solution is characterized by a broad structureless spectrum peaking at 475 nm for PPyr dissolved in TOL as well as in the film cast from these solutions. The distinct similarity of the fluorescence spectra in solution and in solid state provides good evidence for the absence of aggregation in the excited state of the compound which on the one hand stems from the strong steric hindrance caused by the *tert*-butyl-groups at the 7-position and on the other hand is based on the high dihedral angle between two adjacent monomer units [16].
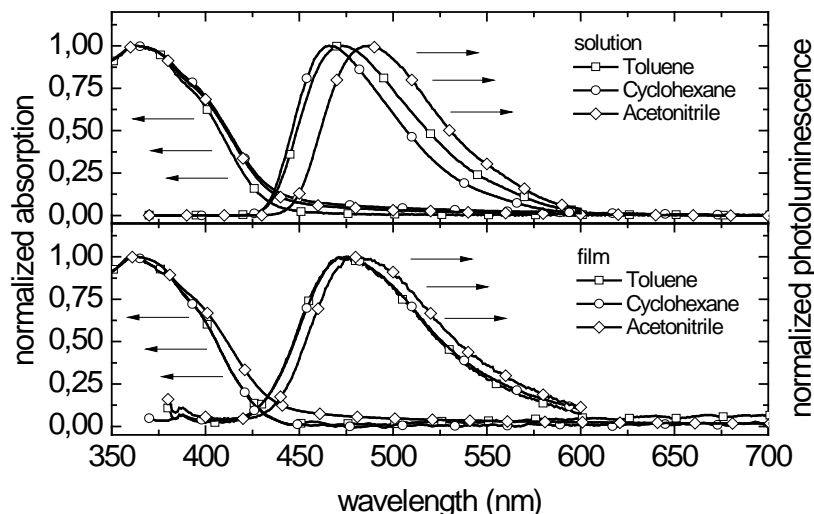
Fig. 2. UV-Visible absorption (360 nm) and photoluminescence emission spectra (466-487 nm) of PPyr in toluene, cyclohexane and acetonitrile (top) and in thin film spin cast from different solutions (bottom).

As documented by many examples in literature, unsubstituted pyrene [18], and macromolecules containing pyrene moieties [19,20] typically display a strong solvatochromic effect as a consequence of the influence of solvent polarity on the molecular conformation. To investigate this influence on the photoluminescence and absorption of PPyr a series of solvents with increasing polarity (CH, TOL and ACN) has been tested. In addition to absorption and emission spectra of dilute solutions also thin films cast from each of the named solvents were investigated. As depicted in Fig. 2, an enhancement of the solvent polarity leads to a bathochromic shift of the PL peak maximum from 466 nm to 487 nm. In the absorption spectra on the contrary no shift of the maxima can be observed, yet the onset of the absorption spectra of the ACN and CH solutions show a minor broadening. Since the respective solutions exhibited a slight turbidity the broadening is attributed to scattering of light by not fully dissolved polymer particles. From a comparison to pyrene dimers having a 1,1-coupling the bathochromic shift can be assigned to the formation of a charge transfer state in solvents with higher polarity, forcing the highly twisted molecules into a more planar structure yielding the observed change of the photoluminescence [20–23]. Remarkably the shift observed in the photoluminescence of different solutions can also be partly found in a series of thin films spin coated from the mentioned solvents. As also depicted in Fig. 2 the photoluminescence spectra of films cast from CH and TOL exhibit a maximum at 475 nm, while the film cast from ACN possesses a maximum at 482 nm. From this observation it is concluded that the conformation of the molecule as found in solution may be also present in the solid state. Here in particular this is of high significance for the fabrication of organic light emitting devices from this polymer since a red-shift of the maximum in the as discussed range results in a shift from the preferable deep blue spectral region to the unpreferable blue-green region.

For light emitting devices not only the emission spectrum is of high importance but also a balanced charge carrier transport to realize efficient devices [24]. To achieve an improved charge carrier transport for holes in the polymer, 3% triphenylamine-groups, known for their good hole transport properties [25] were statistically co-polymerized into the PPyr resulting in the copolymer PPyr/TPA (Fig. 1).

Absorption and photoluminescence spectra of PPyr/TPA in TOL-solution and in thin film are presented in Fig. 3. The absorption maximum can again be found in the range of 360 nm in toluene and in the solid state. The fluorescence maximum is located at 450 nm for the dissolved polymer and the solid states emission maximum is observed around 460 nm for

PPyr/TPA. As already noticed for PPyr, PPyr/TPA shows no sign of an excimer band emission at lower energies.

The fluorescence maxima of 475 nm for PPyr and 460 nm for PPyr/TPA reveal that both polymers exhibit blue fluorescence in the solid state and thus fulfill well the requirement for blue emitting materials. In addition analyses of the fluorescence quantum yield of both pyrene based polymers in toluene solutions resulted in photoluminescence quantum yields (PLQY) of $\Phi_f = 0.88$ for PPyr and $\Phi_f = 0.77$ for PPyr/TPA (quinine sulfate as reference with an excitation wavelength of 360 nm).
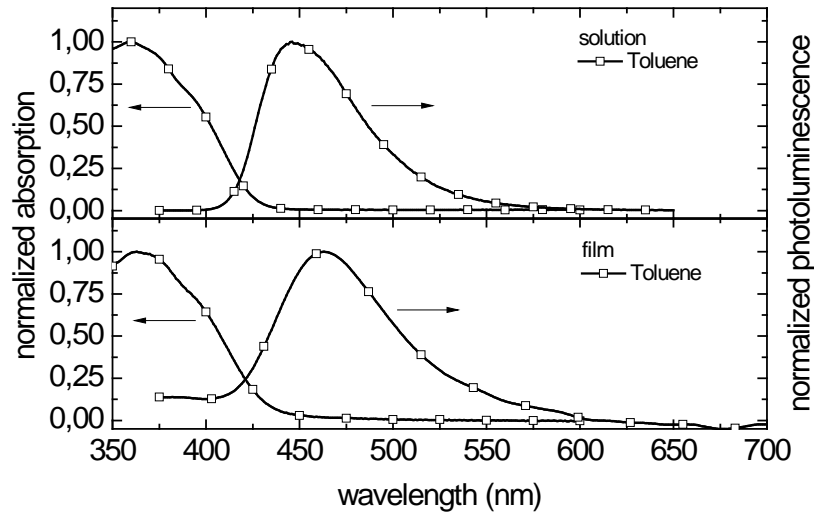

Fig. 3. UV-Visible absorption and photoluminescence emission spectra (λ_{exc} = 360 nm) of PPyr/TPA in toluene (top) and in thin film spin cast from this solution (bottom).

Unsubstituted pyrene molecules are known for their exceptionally long fluorescence lifetimes [11,12], which especially in OLEDs can lead to a high fluorescence quenching rate and consequently to low device efficiencies. In order to elucidate the effect of polymerization of pyrene as compared to a single molecule on the excited states decay dynamics (SE and TE lifetime) TRPL spectra of solutions and thin films of PPyr as depicted in Fig. 4 and PIA spectra as depicted in Fig. 5 have been recorded and evaluated. The results are summarized in Table 1 and compared to literature values obtained for pyrene as well as for other blue emitting conjugated polymers to assess possible non radiative quenching effects of TE in devices.

By TRPL measurements a lifetime τ_f of 1.9 ns is obtained for PPyr in toluene solution. This result presents a completely different decay dynamics of pyrene SEs within the polymer as compared to the single pyrene molecule where a SE-lifetime of 458 ns [13] was measured. Note that we rule out intermolecular excimer emission as the origin of the fluorescence emission for PPyr since no spectral evidence for a low energy emission band is found at the low concentrations of the compound in the solution under investigation ($\sim 1 \times 10^{-3}$ mg/ml). This leads us to the conclusion that polymerizing pyrene in a 1,3-configuration shortens the detected fluorescence lifetime by ca. 200 times, however, still conserving the high PLQY of 88% in solution. Note that very similar results are found when pyrene is incorporated into pyrene-dendrimers [26].

In thin film PPyr exhibits double exponential fluorescence decay with lifetimes τ_f of 27 ps and 146 ps with a relative weight of 65% and 35%, respectively. These results display that the SE lifetimes of PPyr are drastically shorter (ca. 2700 times) than those of pyrene molecules in thin films. As found for solutions with different polymer content [16] also the PL results of films show no evidence for excimer formation.
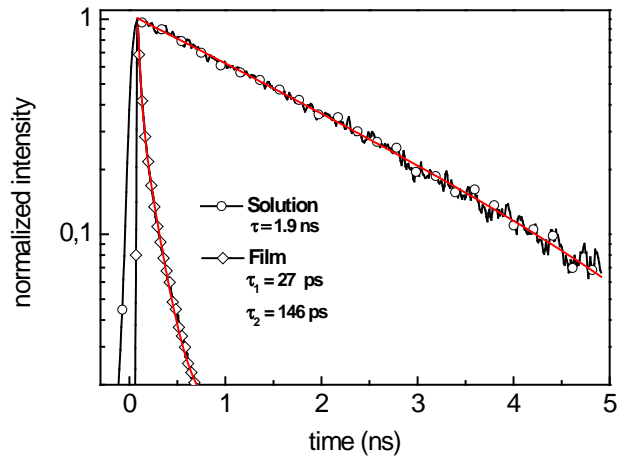
Fig. 4. TRPL decay of a PPyr solution in toluene and of a PPyr thin film (λ_{exc} = 380 nm). Solid lines: mono-exponential (solution) and double-exponential (thin film) fits for fluorescence lifetime evaluation.

The main graph in Fig. 5 shows the PIA spectrum as well as the regular absorption of a PPyr film. The PIA exhibits one broad feature with a maximum at 1.67 eV. From a comparison of this feature in shape and position to other phenylene type polymers [27] this transition is assigned to a triplet-triplet transition T1. In order to determine the lifetime of the T1 transition and hence the TE state dynamic the dependence of the in phase, out of phase and quadrature signals of the lock-in amplifier on the modulation frequency have been measured. Based on the fact that one can directly extract the lifetime of the state k_{TE} from the global maximum of the out of phase component via $k_{TE} = 2\pi * v_{max}$ [28,29], an average TE lifetime of 8.3 ms (v_{max} = 17.82 Hz) is obtained.
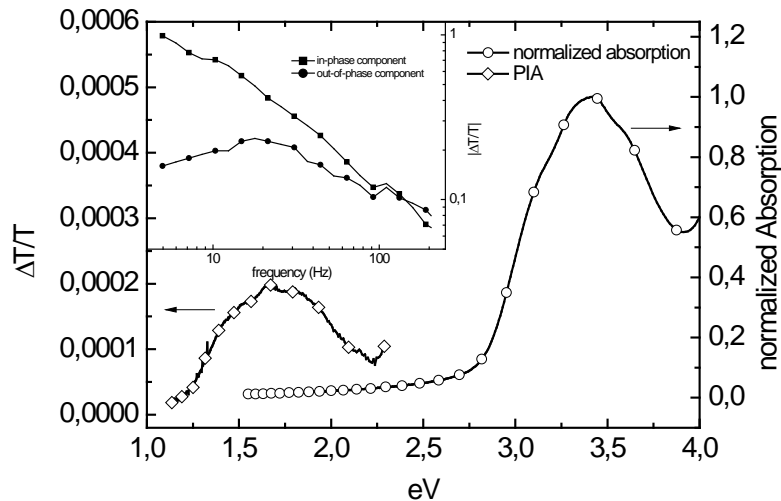

Fig. 5. Normalized absorption spectrum of polypyrene and photoinduced absorption spectrum of PPyr at 100K; inset: absolute value of In-phase- and Out-of-phase component to determine the lifetime of triplet excitons at 760 nm (100mW laserpower, λ_{exc} = 364 nm).

A comparison of the TE lifetimes of isolated pyrene molecules and PPyr in thin films shows a 50 times shorter TE lifetime in the polymer. Consequently it can be expected that conceivable quenching processes of SE by SE-TE annihilation due to long lived TEs

(resulting in a large steady state population of TEs) resulting in a major reduction of the fluorescence quantum yield are of second order in PPyr thin films.

An expansion of the comparison of Table 1 with established values for the well studied blue emitting poly(para-phenylene)(PPP)-type polymers shows in fact that the excited states decay dynamics of PPyr resembles much more that of polyfluorene (PF) than that of the single pyrene molecule. This can in particular be concluded by comparing the SE-TE-lifetime ratio of PPyr and PF in the solid state. Within the error of the experiment these values are located in the same order of magnitude and consequently processes like SE-TE annihilation are expected to be similar in PPyr as compared to PF.

Table 1. Singlet exciton and triplet exciton lifetimes of pyrene-molecule, pyrene-polymer PPyr and polyfluorene in solution and in solid state

	Pyrene Molecule		PPyr			PF	
	solution	*Film*	*solution*	*film*		*solution*	*film*
SE-lifetime	458 ns[a]	400 ns[b]	1.9 ns	146 ps	27 ps	370 ps[c]	170 ps[c]
SE-LT rel. weight	100%	100%	100%	35%	65%	100%	100%
TE-lifetime	9.4 ms[d]	0.45 s[b]	-	8.9 ms		108 µs[e]	2 ms[f]
SE-TE-LT Ratio	$1:2\times10^4$	$1:1\times10^6$	-	$1:6\times10^7$	$1:3\times10^8$	$1:3\times10^5$	$1:1\times10^7$

[a] From J. Chem. Phys. **59**, 801 (1973).
[b] From J. Phys. Chem. **73**, 1747 (1969).
[c] From H.Scheiber, PhD Thesis, unpublished results (2008).
[d] From J. Chem. Phys. **54**, 1 (1971).
[e] From Chem. Phys. **285**, 3 (2002).
[f] From Synth. Met. **139**, 847 (2003).

At that point, however, it should be mentioned that compared to PF PPyr is considered to be chemically more stable than the PPP-type polymer. While both compounds exhibit low TE lifetimes which lower the probability of oxidization of the organic molecules by ground state oxygen, PPyr lacks the instable 9-position of PF which is known for its irreversible formation of on-chain oxidative keto-defects upon phtooxidation [30,31].

In OLEDs an unfavorable energy band alignment of the emitting material with respect to the adjacent layers can significantly lower the device efficiency because of possible charge carrier blocking and subsequent inbalanced charge carrier injection [32]. Consequently it is of particular importance for optimizing the proper OLED configuration to gain knowledge about the corresponding energy levels of the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO) of the light emitting material. To evaluate the energy levels of PPyr UPS measurements were conducted and are presented in the following.

A valence UPS spectrum of PPyr is depicted in Fig. 6. The low binding energy (BE) region of the spectrum shows three prominent features, centered at 1.4 eV, 2.2 eV, and 3.2 eV below the Fermi-level (EF) of the conductive polymer substrate. The lowest BE feature is derived from the highest occupied molecular orbital of the pyrene monomers. The BE onset of this emission feature is at 0.8 eV, and in conjunction with the secondary electron cutoff the ionization energy (IE) of PPyr is 5.6 eV. Noteworthy, the HOMO-derived emission is rather narrow in UPS, which points towards little wavefunction delocalization beyond the pyrene monomer. Typically in polymers with pronounced electronic interaction between individual monomers HOMO-derived bands of several eV width develop, which show up in UPS as flat features [33]. Consequently, the PPyr frontier electronic structure resembles more that typically found for molecular materials rather than for polymers.

As already stated above an efficient charge carrier injection into the emitting layer is decisive for the realization of efficient light emitting devices. In order to observe the suitability of the electron transporting material TPBi for PPyr-based OLEDs UPS

measurements were performed on substrates where the small molecule compound was evaporated incrementally onto the polymer layer. The deposition of TPBi results in a suppression of the PPyr features and in the emergence of two strong peaks (Fig. 6). The BE of the peaks monotonically increases by ca. 0.2 eV/nm up to 5 nm coverage and remains constant for higher thicknesses. The low BE onset of the HOMO-derived TPBi feature is at 1.8 eV below EF, the ionization energy is 6.2 eV (at 5 nm coverage). In contrast, the SECO shifted by 0.4 eV to lower BE, implying an electrostatic potential shift across the PPyr/TPBi interface by −0.4 eV. The reason for this shift is most likely due to TPBi adopting a different conformation right at the interface as compared to the bulk, resulting in a collective effect of intra-molecular dipoles [34]. Pinning of EF at the TPBi interface induced gap states or impurity levels is improbable because of the substantial energy separation between the TPBi frontier levels and EF.
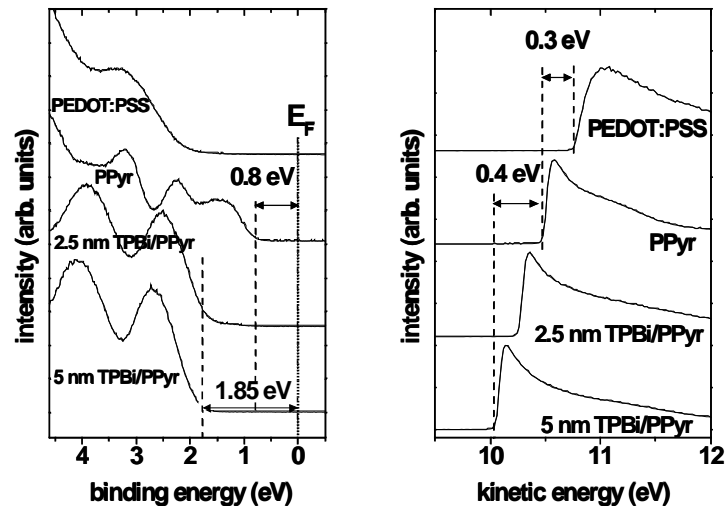

Fig. 6. Valence region UPS- (left) and SECO (right) spectra of PEDOT:PSS, pure polypyrene and of PPyr covered by 2.5 nm and 5 nm thick layer of TPBi.

The energy levels across the PEDOT:PSS/PPyr/TPBi interfaces are summarized in Fig. 7. As can be observed the positions of corresponding energy levels of TPBi seem to be well suited for an OLED application with PPyr. This can be concluded firstly because the electron affinity of the electron transporting TPBi is located at lower energy compared to the polymer thus forming no energy barrier at the PPyr/TPBi interface for electrons injected from the cathode. Secondly the high ionization potential of TPBi generates a blocking energy barrier for positive charges at the interface to the emitting layer hence constraining their extraction. These properties should be leading to high charge carrier densities in the active polymer layer which are necessary for high recombination densities [24].
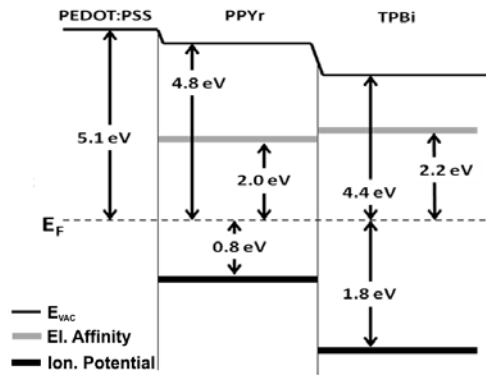
Fig. 7. Energy level diagram for PEDOT:PSS/PPYr/TPBi.

To finally investigate the electroluminescent properties of PPyr and their spectral stability over time PLEDs were fabricated in a standard sandwich geometry using the following assembly: ITO/ PEDOT:PSS/ PPyr/ TPBi/ Ca/ Al. TPBi was used at the cathodes side since it is known for its electron transporting and hole blocking abilities [35,36]. Additionally possible interface defect-states at the emitting layer/Ca-interface [37] should be prevented by the small molecules.

Figure 8a shows the current density-voltage-luminance (J-V-L) characteristics of a device with PPyr as emitting layer. The PLED exhibited a deep blue electroluminescence emission achieving a maximum luminance of 1043 cd/m^2 at a bias of 6.2 V, which is a threefold improvement compared to the first publication on that material [16]. The device showed a fairly low onset of the electroluminescence at 3.2 V and a maximum efficiency of 0.12 cd/A was reached. This rather limited device efficiency is assigned to an unbalanced charge transport in the active polymer. The electroluminescence spectrum depicted in the inset of Fig. 8a shows a structureless molecular emission peak between 430 nm and 550 nm with its maximum at 460 nm. This corresponds to Commission Internationale de l'Eclairage 1931 (CIE1931) coordinates of x = 0.158 and y = 0.176, thus resulting in a deep blue emission. Both, shape and maximum of the EL-emission are very similar to the PL-spectrum in thin film, showing no signs of often observed excimer emission. This again provides definite evidence for the effective suppression of molecular aggregation due to the *tert*-butyl groups attached to the 7-position. Furthermore the inset of Fig. 8a presents the development of the EL-emission during continuous operation with a current density of 1.11 kA/m^2. As can be observed the material did not show a significant spectral change during the time of five minutes.

PLEDs with PPyr/TPA as emitting layer were fabricated in the same assembly as for PPyr: ITO/ PEDOT:PSS/ PPyr/TPA/ TPBi/ Ca/ Al. Due to the implementation of the TPA-groups the hole transport mobilities were expected to be improved therefore the overall device efficiencies should be considerably enhanced compared to PLEDs containing pure PPyr. Figure 8b depicts the J-V-L characteristics of a PPyr/TPA device. Again a deep blue electroluminescence emission was observed with a maximum brightness of 1035 cd/m^2 at a bias of 6.2 Volts. An onset bias of 3.8 V was detected and the maximum efficiency yield 0.19 cd/A at 6,4 V. A comparison to the peak efficiency of the PPyr device clearly demonstrates that only a small amount of TPA-groups was sufficient to enhance the device efficiency considerably. EL-spectra shown in the inset of Fig. 8b at turn-on as well as during operation at a current density of 1.11 kA/m^2 reveal once more the exceptional spectral stability of the material. A molecular emission peak in the range between 420 nm and 540 nm was detected with its maximum at 450 nm, corresponding to CIE1931 coordinates of x = 0.155 and y = 0.141 located clearly in the deep blue region of the visible spectrum.
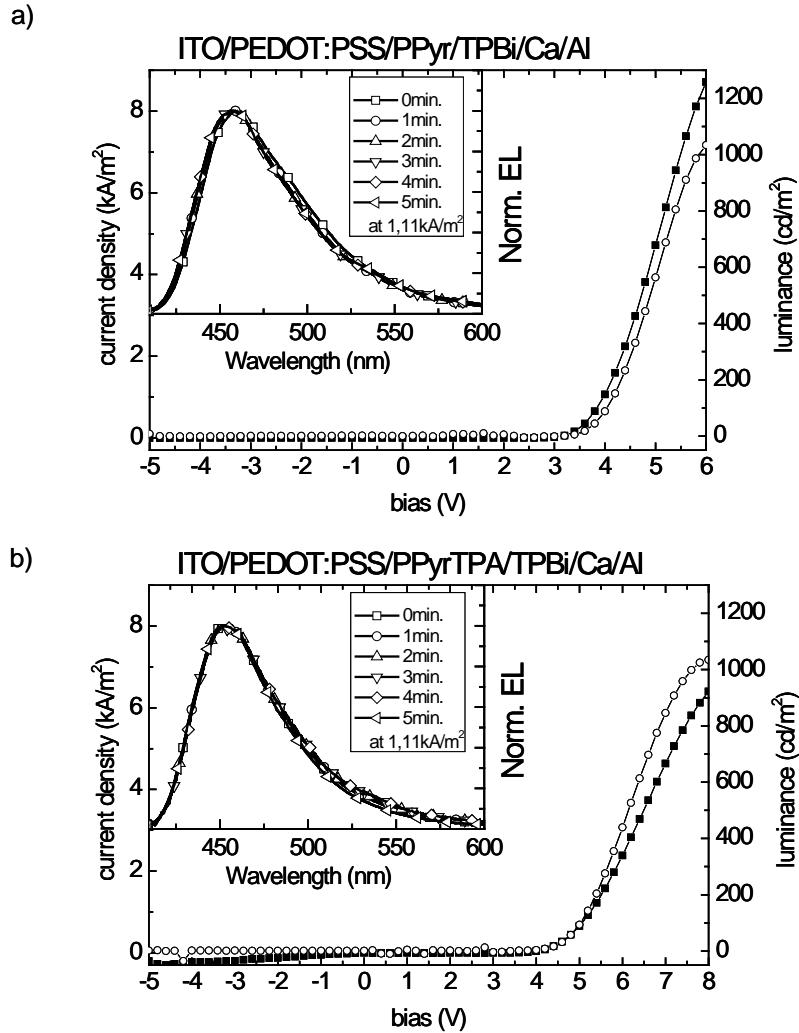
a)

b)

Fig. 8a. Current density (line with squares) / luminance (line with circles) as a function of the bias voltage in an ITO/PEDOT:PSS/PPyr/TPBi/Ca/Al device. The inset shows the electroluminescence emission spectrum after 1–5 minutes of continuous operation for the same device. The emission spectra have been obtained at a current density of 1.11 kA/m^2 and a bias of ca. 4.1 V. Figure 8b: Current density (line with squares) / luminance (line with circles) as a function of the bias voltage in an ITO/PEDOT:PSS/PPyrTPA/TPBi/Ca/Al device. The inset shows the electroluminescence emission spectrum after 1–5 minutes of continuous operation for the same device. The emission spectra have been obtained at a current density of 1.11 kA/m^2 and a bias of ca. 5.3 V.

7. Conclusion

In conclusion we demonstrated detailed photo-physical investigations on a novel easy to synthesize non aggregating class of pyrene based polymers. PPyr and PPyr/TPA exhibit deep blue fluorescent light emission and results from PL-measurements show that neither in solution nor in thin film a sign of polymer aggregation and resulting excimer emission can be found. Additionally high photoluminescence quantum yields of 88% for PPyr and 77% for PPyr/TPA could be measured. The influence of the solvents polarity on the photoluminescence spectrum is demonstrated to play a significant role to prevent possible charge transfer states within the materials causing an unwanted red-shift of the emission.

TRPL- and PIA-measurements revealed that SE and TE lifetimes are significantly reduced compared to the single pyrene molecule and in thin film the lifetimes are in the same order of magnitude as in well known PPP-type polymers like polyfluorene. UPS measurements show only little inter-monomer wavefunction delocalization. Consequently the high dihedral angle between two adjacent monomer units not only hinders the interaction of different polymer chains, preventing excimer emission, but also limits the electronic interaction between different monomers on the same chain. Moreover highly luminescent polymer light emitting devices were realized using an improved assembly with TPBi as electron transporting material exhibiting a bright deep blue and stable electroluminescence emission and the possibility to further improve the device's efficiency by copolymerizing triphenylamine groups at a monomer ratio of 3% into the polymer backbone was demonstrated.