## Investigation of Spacer Influences in Phosphorescent-Emitting Nonconjugated PLED Systems

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ABSTRACT: An assay was introduced to clarify influences on electroluminescent behavior for RGB-colored phosphorescent terpolymers with *N,N*-Di-*p*-tolyl-aniline as hole-transporting unit, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (*tert*-BuPBD) as electron-transporting unit, and different iridium complexes in RGB-colors as triplet emitting materials. All monomers were attached with spacer moieties to the "para" position of a polystyrene. Polymer light emitting diodes (PLEDs) were built to study the electro-optical behavior of these materials. The gist was a remarkable influence of hexyl-spacer units to the PLED performance. For all three colors only very restricted PLED performances were found. In comparison RGB-terpolymers were synthesized with directly attached charge transport materials to the polymer backbone. For this directly linked systems efficien-

**INTRODUCTION** Since Burroughes et al.<sup>1</sup> reported the first discovery of a PLED in 1990, these materials became more and more attractive because of cost efficiency and ease processing by printing techniques from solution. Large area displays or plane lighting with light emitting polymers printed via ink-jet<sup>2</sup> or roll-to-roll<sup>3</sup> processes are now conceivable. The use of phosphorescent organometallic complexes of transition metals and their chromophoric ligands show higher quantum efficiencies compared to singlet emitting materials.<sup>4</sup> Light emissions of conjugated polymers like polyfluorene or polyvinylenephenylene, generated by fluorescence, are restricted by spin statistics to efficiencies of 25%. Some transition metal complexes, first to name cyclometalated iridium-(III) complexes, provide very short triplet lifetimes of excited states that up to 100% efficiencies of these systems in adapted matrices are possible.<sup>5</sup> Several attempts have been applied to establish triplets in polymeric, respectively soluble matrices for example, poly(N-vinylcarbazole) (PVK) as a nonconjugated, redox-active matrix.<sup>6,7</sup> Yang et al.<sup>8,9</sup> achieved high efficient and bright PLEDs by blending the PVK-matrix with iridium-(III) complexes, electron-, and additional hole-transporting molecules. The wide bandgap of PVK (ca. 3.7 eV) allows different emission colors without any interaction between the active components and the polymer matrix. Furthermore, conjugated

cies were 28 cd  $A^{-1}$  @ 6 V (green), 4.9 cd  $A^{-1}$  @ 5 V (red) and 4.3 cd  $A^{-1}$  @ 6 V (bluish). In summary we assume that an improved charge percolation pathways regarding to the higher content of semiconducting molecules and an improved charge transfer to the phosphorescent dopand in the case of the copolymers without spacers are responsible for the better device performance comparing the copolymers with hexyl spacers. The approach of the directly connected charge transport materials at the nonconjugated styrene polymer backbone should be favored for further investigations, therefore. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 389–402, 2010

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polymers, especially polyfluorenes, were applied as host systems for triplet emitters.<sup>10–13</sup> Efficient PLEDs were obtained for the colors green and red, but not for blue because of interactions with the polymer matrix emission.<sup>14</sup> The bandgap of these conjugated polymers is lower than 3 eV. To prevent phase separation, Evans et al.<sup>15</sup> reported the introduction of spacer groups into a polyfluorene host matrix to the phosphorescent dopand. They used a red emitting iridium-(III) complex with 2-(2'benzo[*b*]thienyl)pyridinato-ligands (btp) and tethered it at the 9-position of 9-octylfluorene with an octyl-spacer moiety. With this approach they avoided a triplet energy transfer from the red phosphorescent iridium complex to the polyfluorene backbone and, thereby, achieved an augmentation of the photoluminescence intensity. Graf et al.<sup>16</sup> established an iridium-(III) complex with 2-phenylpyridinato (ppy) chromophoric ligands and the saturation ligand acetylacetonate connected to one hexyl moiety of 1,4-dibromo-2,5bis(hexyloxy)benzene. This is another example of a nonconjugated connection of phosphorescent materials into a conjugated polymer matrix system using spacer moieties. Dendrimers were introduced to realize charge transport materials with adequate film building properties.<sup>17-19</sup> According to the wide bandgap of dendronic hosts (>4 eV), it was possible to cover the full visible range.

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An alternative strategy to eliminate phase separation in polymer systems is to introduce a nonconjugated covalent linkage between phosphorescent dopands and nonconjugated polymer hosts. In such matrix systems the polymer backbone does not take place in charge transport or emission because of its extremely high bandgap of more than 4 eV. The usage of this kind of linkage realizes an unlimited mixing of active side groups and causes a stable morphology, since migration and aggregation is suppressed very hard by fixing the active molecules as side groups. Nonconjugated polymer matrices are on principle much better soluble in common solvents, compared to conjugated polymers, what alleviate their application to solution processed PLEDs. Polystyrene is known to be a relatively chemically inert and optical stable polymer material. Therefore, Suzuki et al.<sup>20</sup> reported a polymer matrix system based on polystyrene with covalently fixed electron- and hole-transporting side functionalities. To avoid phase separation and degradation the iridium complex was also attached to the polystyrene backbone and for these optimized systems external quantum efficiencies up to 12% were observed.

#### **EXPERIMENTAL**

#### **Materials and Methods**

All materials were obtained from Aldrich Chemical Company or Acros Organics and used without any further purification unless otherwise stated. THF for polymerization reactions was freshly distilled over sodium and stored under nitrogen. Silica gel 60 (Merck) and C18 reversed phased silica gel (Merck) was used in the separation and purification of compounds by column chromatography. Solvents for column chromatography, recrystallization and purification were received from Th. Geyer GmbH and J. T. Baker. High-resolution (500 MHz) <sup>1</sup>H NMR spectra were recorded using a UNITY INOVA 500 spectrometer from Varian. Elemental analyzes were obtained using a Thermo Scientific FlashEA 1112 CHNS/O Automatic Elemental Analyser. For the iridium analyzes, 10 mg of each sample were solved into 1 mL of nitric acid 65% (Merck) and 1 mL of perchloric acid 70%, and subsequently radiated in a microwave oven PAAR Physica Multiwave for 30 min. The sample was diluted with water to 15 mL and analyzed with a ICP-OES Optima 2100 DV using iridium standards (Merck). Gel-permeation chromatography (GPC) at 25 °C in THF was used to determine the molecular weight. For this purpose a combination of a Waters HPLC-Pump 515, Autosampler 717 plus, Dual l Absorbance Detector 2487 and a Refrative Index Detector 2414 was used. A precolumn and three columns from Waters (7.8 mm  $\times$  300 mm; Styragel HR3, HR4, HR5), filled with a copolymer of styrene and divinylbenzene 5 µm and PS-Standards from Polymer Laboratories (Varian), were used. The polymer solution (2 mg  $L^{-1}$  in THF) stirred for 24 h at room temperature and filtered through a syringe PTFE filter 1  $\mu$ m, before 2  $\times$  100  $\mu$ L of each polymer-solution were injected. Molecular weights were calculated with the Empower software from Waters. Thermal analysis was performed with differential

UV/vis spectra were recorded with a Perkin–Elmer Lambda 950 spectrometer at room temperature as dropcasted films on silica glass substrates. Therefore, the polymer solution from THF was dropcasted on silica glass substrates, to perform layer thicknesses between 400 and 500 nm after the evaporation of the solvent at room temperature. Photoluminescence spectra were measured using a Perkin–Elmer LS50B spectrometer and the mentioned dropcasted films.

#### **CV Measurements**

Voltammograms were obtained using an EG&G Parc model 273 potentiostat, controlled by an IBM P70 computer. A three electrode configuration was applied, contained in an undivided cell consisting of a glassy carbon electrode (area  $0.5 \text{ cm}^2$ ) where the polymer film was deposited, a platinum mesh as the counter electrode, and an Ag/AgCl (3 M NaCl and sat. AgCl) reference electrode. 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile was used as electrolyte and prior each measurement the electochemical cell was deoxygenated with nitrogen. Furthermore, the electrochemical cell was calibrated by the use of a ferrocene standard and the ferrocene half-wave potential was estimated to 435 mV for this assembly. 1 wt % polymer solutions in chloroform were prepared and 5  $\mu$ L were deposited at a glassy carbon electrode. The prepared electrodes were kept under vacuum and dried at 60 °C for 2 h. For measurements in solution a platinum disc was used as working electrode and the concentrations of organic compounds in the electrolyte system were close to  $10^{-3}$  mol L<sup>-1</sup>.

#### **Device Fabrication**

The transparent indium-tin-oxide (ITO) covered glass slides were received from OPTREX Europe GmbH (sheet resistance 20  $Ohm/\Box$ ) and were chemical wet cleaned in an ultra sonic bath before use. The hole injecting layer was polyethylenedioxythiophene doped with polystyrenesulphonic acid (CH8000, H.C. Starck) and dried at temperatures above 130 °C for 5 min to remove the solvent residues, followed by a spin-coating process of the emitting polymer solution from chlorobenzene to receive polymer layer thicknesses of about 60 to 80 nm after another annealing step for 10 min at 110 °C. In advance, the polymer solutions were solved before for 24 h at room temperature in chlorobenzene, using a shaker. Subsequently, they were filtered through PTFE-syringe filters with pore sizes of 0.2  $\mu$ m. The cathodes (CsF 4 nm; Ca 15 nm; Ag 50 nm) were assembled by a thermal evaporation process at pressures below  $10^{-5}$  Pa. Four devices of each polymer were build to guarantee uniformity. The complete sample preparation and measurements were carried out in a clean room under nitrogen atmosphere. Device characterisation: The current-voltage and the luminance-voltage characteristics of the devices were measured simultaneously with a computer controlled Keithley 236 Source-Measure-Unit in combination with an Optometer Model GO352, equipped with a calibrated sensor head for the luminance measurements. The electroluminescence spectra were recorded in a glove box system under nitrogen atmosphere with a diodearray Spectrometer EPP 2000 from Stella Net.

#### Synthesis

## 4-Methyl-N-p-tolyl-N-(4-vinylphenyl)aniline (2)

Methyl triphenyl phosphonium bromide (1.48 g; 4.14 mmol) was weighed into a round-bottom flask with septum. The apparatus was evacuated and flushed with Ar three times. 15 mL of dry THF were added and the mixture was cooled to 0 °C. n-BuLi (1.6 *M* in hexane; 2.6 mL; 4.14 mmol) was injected slowly and the mixture stirred for 10 min at 0 °C to perform a slightly yellow liquid. A solution of *N*,*N*-bis(4-methylphenyl)-aminobenzaldehyde **1** (0.50 g; 1.66 mmol) in 10 mL THF was injected drop wise and the reaction mixture stirred at room temperature for 2 h.  $CH_2Cl_2$  was added and the solution washed several times with water, dried with  $Na_2SO_4$ , filtered and concentrated. Column chromatography with 10:1 hexane/ethyl acetate as eluant gave 0.42 g (85%) **2** as slight yellow solid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.24 (d, J = 8.6 Hz, 2H, ArH), 7.05 (d, J = 8.5 Hz, 4H, ArH), 6.98 (d, 4H, ArH), 6.96 (d, 2H, ArH), 6.63 (dd, J = 10.8 Hz, 17.6 Hz, 1H, ArCHCH<sub>2</sub>), 5.60 (d, 1H, CHCH<sub>2</sub>), 5.11 (d, 1H, CHCH<sub>2</sub>), 2.30 (s, 6H, CH<sub>3</sub>). Anal. calcd. for C<sub>22</sub>H<sub>21</sub>N ( $M_w$  299.41 g mol<sup>-1</sup>): C 88.25, H 7.07, N 4.68; found: C 88.46, H 6.99, N 4.55.

#### 2-(6-Bromohexyloxy)tetrahydro-2H-pyran (4)

6-bromohexane-1-ol (35 g; 0.19 mol) and some *p*-toluenesulphonic acid crystals were dissolved in 60 mL of dry toluene. 3,4-Dihydropyrane (30 mL, 0.33 mol), solved in 40 mL of dry toluene were injected drop wise. The mixture was heated to 100 °C and stirred for 4 h.  $K_2CO_3$  (4.7 g; 34.0 mmol) was added and the mixture allowed to stir at room temperature over night. Afterwards, the liquid phase was separated and concentrated. Column chromatography with hexane/ethyl acetate 10:1 gave the pure product **4** 35.62 g (71%) as slight yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.54 (m, 1H, OCHO), 3.83 (m, 1H, OCH<sub>2</sub>-pyrane), 3.70 (m, 1H, OCH<sub>2</sub>-alkyl), 3.47 (m, 1H, OCH<sub>2</sub>-pyrane), 3.36 (t, 2H, CH<sub>2</sub>OH), 3.34 (m, 1H, OCH<sub>2</sub>-alkyl), 1.84 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>OH), 1.80 (m, 1H, CHCH<sub>2</sub>), 1.67 (m, 1H, CHCH<sub>2</sub>), 1.6...1.35 (m, alkyl chain). Anal. calcd. for C<sub>11</sub>H<sub>21</sub>BrO<sub>2</sub> ( $M_w$  265.19 g mol<sup>-1</sup>): C 49.82, H 7.98; found: C 49.69, H 7.84.

#### 6-(4-(Di-p-tolylamino)phenyl)hexan-1-ol (5)

**3** (5.76 g; 16.4 mmol) was loaded into a round-bottom flask with septum and the apparatus was evacuated and flushed with Ar three times. 80 mL of dry THF and 80 mL of dry hexane were added and the mixture was cooled to -78 °C. n-BuLi (1.6 *M* in Hexane; 10.25 mL, 16.4 mmol) was injected slowly and the mixture stirred for 45 min at -78 °C. **4** (4.77 g; 18.0 mmol) was added and the reaction mixture was allowed to stir at room temperature for 16 h. Afterwards, the solution was diluted with diethyl ether, washed several times with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated. The raw product was solubilized in 20 mL THF and 20 mL 2 *N* HCl and stirred at 50 °C for 2 h. The separated

organic phase was washed several times with water, dried over  $Na_2SO_4$ , filtrated and concentrated. Column chromatography with hexane/ethyl acetate 1:1 gave 5 as a slight yellow oil 4.94 g (81%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.02 (m, 6H, ArH), 6.96 (m, 6H, ArH), 3.64 (t, J = 6.6 Hz, 2H,  $CH_2$ OH), 2.54 (t, J = 7.8 Hz, 2H, ArC $H_2$ ), 2.30 (s, 6H,  $CH_3$ ), 1.58 (m, 4H, alkyl chain), 1.39 (m, 4H, alkyl chain). Anal. calcd. for C<sub>26</sub>H<sub>31</sub>NO ( $M_w$  373.53 g mol<sup>-1</sup>): C 83.60, H 8.37, N 3.75; found: C 83.42, H 8.33, N 3.69.

# Di-p-tolyl-{4-[6-(4-vinyl-benzyloxy)-hexyl]-phenyl}-amin (6)

Small portions of Na (0.16 g; 6.68 mmol) were weighed into a round-bottom flask with septum. The apparatus was evacuated and flushed with Ar three times. **5** (2.50 g; 6.68 mmol) in 20 mL THF was added and the mixture was stirred for 16 h at reflux. 1-chloromethyl-4-vinyl-benzene (1.15 g; 7.53 mmol, technical, purified before with silica gel 60) was injected and the mixture stirred another 16 h at reflux temperature. The mixture was diluted with diethyl ether, washed several times with water, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Column chromatography over RP-18 KG with acetone/water 10:1 gave **6** as slight yellow oil 2.0 g (61%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.32 (d, 2H, ArH), 7.04 (m, 6H, ArH), 6.98 (m, 6H, ArH), 6.73 (dd, J = 10.8 Hz, 17.6 Hz 1H, ArCHCH<sub>2</sub>), 5.76 (d, 1H, CHCH<sub>2</sub>), 5.25 (d, 1H, CHCH<sub>2</sub>), 4.51 (s, 2H, ArCH<sub>2</sub>O), 3.48 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>O), 2.56 (t, J = 7.7 Hz, 2H, ArCH<sub>2</sub>), 2.32 (s, 6H, CH<sub>3</sub>), 1.63 (m, 4H, alkyl chain), 1.40 (m, 4H, alkyl chain). Anal. calcd. for C<sub>35</sub>H<sub>39</sub>NO ( $M_w$  489.69 g mol<sup>-1</sup>): C 85.84, H 8.03, N 2.86; found: C 85.52, H 7.98, N 2.77.

## 2-[4-(4'-Acetylbiphenylyl)-5-(4-tert-butylphenyl)]-1,3,4-oxadiazole (8)

*tert*-BuPBD **7** (11.5 g; 32.4 mmol) was dissolved in 300 mL of dry  $CH_2Cl_2$ . Freshly distilled acetyl chloride (5.8 mL; 82.0 mmol) and AlCl<sub>3</sub> (32.0 g; 0.24 mol) were added. The mixture was heated to reflux for 5 h. The cooled mixture was slowly poured into 300 mL ice/water and 50 mL concentrated HCl. The separated organic phase was washed three times with water and dried with  $Na_2SO_4$ . After removal of the solvent, the raw product was crystallized in EtOH/CHCl<sub>3</sub> to obtain 10.0 g (78%) **8** as slight yellow crystals.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.25 (d, J = 8.6 Hz, 2H, biphenyl), 8.09 (d, J = 8.6 Hz, 2H, ArH), 8.08 (d, 2H, biphenyl), 7.80 (d, J = 8.6 Hz, 2H, biphenyl), 7.76 (d, 2H, ArH), 7.57 (d, 2H, biphenyl), 2.67 (s, 3H, COCH<sub>3</sub>), 1.38 (s, 9H, CH<sub>3</sub>). Anal. calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> ( $M_w$  396.48 g mol<sup>-1</sup>): C 78.76, H 6.10, N 7.07; found: C 78.29, H 6.39, N 6.54.

## 2-[4-(4'-(1-Hydroxyethyl)biphenylyl)]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (9)

**8** (4.52 g; 11.4 mmol) and NaBH<sub>4</sub> (1.02 g; 27.0 mmol) were dissolved in 100 mL EtOH and stirred at room temperature for 5 h. 2 *N* HCl was added until no more gasification could be observed. The mixture was diluted with CHCl<sub>3</sub>, washed three times with water and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal

of the solvent, 4.40 g (97%) of  ${\bf 9}$  were obtained as slight yellow crystals.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.19 (d, J = 8.6 Hz, 2H, biphenyl), 8.08 (d, J = 8.6 Hz, 2H, ArH), 7.74 (d, 2H, biphenyl), 7.64 (d, J = 8.2 Hz, 2H, biphenyl), 7.56 (d, 2H, ArH), 7.50 (d, 2H, biphenyl), 4.98 (q, J = 6.5 Hz, 1H, CHOH), 1.55 (d, 3H, CH<sub>3</sub>), 1.38 (s, 9H, CH<sub>3</sub>). Anal. calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> ( $M_w$  398.50 g mol<sup>-1</sup>): C 78.36, H 6.58, N 7.03, O 8.03; found: C 78.51, H 6.65, N 7.06, O 8.03.

## 2-[4-(4'-Vinylbiphenylyl)]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (10)

**9** (4.38 g; 11.0 mmol) and *p*-toluenesulfonic acid mono hydrate (0.22 g; 1.15 mmol) were dissolved in 150 mL toluene and the mixture was heated to reflux in a Dean-Stark apparatus for 5 h to remove azeotropic toluene/water. The mixture was concentrated and final column chromatography with hexane/ethyl acetate 4:1 gave 2.18 g (52%) **10** as white pellet crystals.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.20 (d, J = 8.8 Hz, 2H, biphenyl), 8.07 (d, J = 8.8 Hz, 2H, ArH), 7.80 (d, 2H, biphenyl), 7.66 (d, J = 8.3 Hz, 2H, biphenyl), 7.59 (d, 2H, ArH), 7.54 (d, 2H, biphenyl), 6.78 (dd, J = 10.7 Hz, 17.6 Hz, 1H, CHCH<sub>2</sub>), 5.84 (d, 1H, CHCH<sub>2</sub>), 5.31 (d, 1H, CHCH<sub>2</sub>), 1.37 (s, 9H, CH<sub>3</sub>). Anal. calcd. for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O ( $M_w$  380.48 g mol<sup>-1</sup>): C 82.07, H 6.36, N 7.36, O 4.21; found: C 82.32, H 6.38, N 7.34, O 4.40.

#### Ethyl 4'-hydroxybiphenyl-4-carboxylate (12)

11 (10.00 g; 46.7 mmol) was diluted in 170 mL EtOH and 5 mL  $H_2SO_4$ . The mixture was stirred for 5 h at 100 °C. The reaction mixture was dropped into saturated NaHCO<sub>3</sub> (aq.) and the precipitation was filtered and washed with water. After recrystallization from hexane, 9.66 g (85%) of 12 were obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.09 (d, J = 8.4 Hz, 2H, biphenyl), 7.61 (d, 2H, biphenyl), 7.53 (d, J = 8.6 Hz, 2H, biphenyl), 6.94 (d, 2H, biphenyl), 5.14 (s, 1H, OH), 4.40 (q, J = 7.1 Hz, 2H, OCH<sub>2</sub>), 1.42 (t, 3H, CH<sub>3</sub>). Anal. calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> ( $M_w$  242.27 g mol<sup>-1</sup>): C 74.36, H 5.82; found: C 74.21, H 5.88.

#### Ethyl 4'-(6-hydroxyhexyloxy)biphenyl-4-carboxylate (13)

**12** (9.42 g; 38.9 mmol) was dissolved into 150 mL of dry DMF.  $K_2CO_3$  (7.24 g; 52.4 mmol) and some crystals of KJ were added and the mixture was stirred under nitrogen atmosphere at reflux. After the injection of 6-Bromo-hexanole (11.83 g; 65.3 mmol) the mixture was stirred for 3 h at reflux. The reaction mixture was poured into water and the precipitation filtered. After recrystallization from EtOH, 8.55 g (64%) of **13** were obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.07 (d, J = 8.5, 2H, biphenyl), 7.61 (d, 2H, biphenyl), 7.56 (d, J = 8.8 Hz, 2H, biphenyl), 6.98 (d, 2H, biphenyl), 4.39 (q, J = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 4.01 (t, J = 6.6 Hz, 2H, ArOCH<sub>2</sub>), 3.67 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>OAr), 1.83 (m, 2H, alkyl chain), 1.62 (m, 2H, CH<sub>2</sub>OH), 1.54 (m, 2H, alkyl chain), 1.45 (m, 2H, alkyl chain), 1.41 (t, 3H,  $CH_3$ ). Anal. calcd. for  $C_{21}H_{26}O_4$  ( $M_w$  342.43 g mol<sup>-1</sup>): C 73.66, H 7.65; found: C 73.98, H 7.41.

#### 4'-(6-Hydroxyhexyloxy)biphenyl-4-carbohydrazide (14)

13 (2.00 g; 5.84 mmol) was dissolved into 50 mL of isopropanol and heated to 60  $^{\circ}$ C. Hydrazine hydrate (8.5 mL; 0.17 mol) was added drop wise and the mixture was stirred at reflux for 48 h. The precipitation was filtered and washed with water. After crystallization from MeOH 1.59 g (83%) 14 were obtained.

<sup>1</sup>H NMR (500 MHz, Aceton-d<sub>6</sub>,  $\delta$ ): 7.94 (d, J = 8.3 Hz, 2H, biphenyl), 7.70 (d, 2H, biphenyl), 7.66 (d, J = 8.8 Hz, 2H, biphenyl), 7.04 (d, 2H, biphenyl), 4.06 (t, J = 6.5 Hz, 2H, ArOCH<sub>2</sub>), 3.54 (t, J = 6.5 Hz, 2H, CH<sub>2</sub>OH), 1.81 (m, 2H, alkyl chain), 1.54 (m, 2H, CH<sub>2</sub>OH), 1.52 (m, 2H, alkyl chain), 1.46 (m, 2H, alkyl chain). Anal. calcd. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub> ( $M_w$  328.41 g mol<sup>-1</sup>): C 69.49, H 7.37, N 8.53; found: C 69.49, H 7.37, N 8.53.

## 4-tert-Butylbenzoyl Chloride (15)

4-*tert*-Butylbenzoic acid (5.00 g; 28.1 mmol) was placed into a round-bottom flask with septum, evacuated and flushed three times with Ar before. Thionyl chloride (14.2 mL; 0.20 mol) was added and the mixture was stirred at 85 °C over night. Vacuum distillation leads to 3.96 g (72%) of the pure product **15**. Anal. calcd. for C<sub>11</sub>H<sub>13</sub>ClO ( $M_w$  196.67 g mol<sup>-1</sup>): C 67.18, H 6.66; found: C 67.11, H 6.69.

### N'-(4-tert-Butylbenzoyl)-4'-(6-hydroxyhexyloxy)biphenyl-4carbohydrazide (16)

**14** (1.10 g; 3.35 mmol) was dissolved into 17 mL of pyridine and a solution of **15** (0.66 g; 3.35 mmol) in 7 mL of THF was added drop wise under stirring. The reaction mixture was stirred for 54 h at room temperature, poured into 130 mL of 5 N HCl and the white precipitate was filtered and washed with water. After recrystallization from EtOH, 1.25 g (76%) of **16** were obtained.

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 10.52 (s, 1H, N*H*), 10.45 (s, 1H, O*H*), 7.99 (d, *J* = 8.3 Hz, 2H, biphenyl), 7.88 (d, *J* = 8.6 Hz, 2H, ArH), 7.78 (d, 2H, biphenyl), 7.70 (d, *J* = 8.8 Hz, 2H, biphenyl), 7.54 (d, 2H, ArH), 7.05 (d, 2H, biphenyl), 4.02 (t, 2H, C*H*<sub>2</sub>OAr), 3.40 (m, 2H, C*H*<sub>2</sub>OH), 1.74 (m, 2H, alkyl chain), 1.45 (m, 4H, alkyl chain), 1.36 (m, 2H, alkyl chain), 1.32 (s, 9H, C*H*<sub>3</sub>). Anal. calcd. for C<sub>30</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub> (*M*<sub>w</sub> 488.62 g mol<sup>-1</sup>): C 73.74, H 7.43, N 5.73; found: C 73.40, H 7.68, N 5.78.

## 6-(4'-(5-(4-tert-Butylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yloxy)hexyl Acetate (17)

**16** (1.60 g; 3.27 mmol), acetic acid anhydride (12.7 mL; 0.13 mol) and 3 drops of  $H_2SO_4$  conc. were stirred for 2 h at 100 °C. The mixture was precipitated into ice/water and extracted with CHCl<sub>3</sub>. The organic phase was separated, washed several times with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated. Column chromatography with hexane/ ethyl acetate 1:1 gave the pure product (0.43 g; 25%) as white crystals.

<sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ,  $\delta$ ): 8.18 (d, J = 8.3 Hz, 2H, biphenyl), 8.08 (d, J = 8.4 Hz, 2H, ArH), 7.72 (d, 2H,

biphenyl), 7.60 (d, J = 8.7 Hz, 2H, biphenyl), 7.56 (d, 2H, ArH), 7.01 (d, 2H, biphenyl), 4.09 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>OCO), 4.02 (t, J = 6.4 Hz, 2H, CH<sub>2</sub>OAr), 2.06 (s, 3H, CH<sub>3</sub>), 1.84 (m, 2H, alkyl chain), 1.68 (m, 2H, alkyl chain), 1.54 (m, 2H, alkyl chain), 1.47 (m, 2H, alkyl chain), 1.37 (s, 9H, CH<sub>3</sub>). Anal. calcd. for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub> ( $M_w$  512.64 g mol<sup>-1</sup>): C 74.97, H 7.08, N 5.46; found: C 74.85, H 7.06, N 5.42.

## 6-(4'-(5-(4-tert-Butylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yloxy)hexan-1-ol (18)

**17** (0.50 g; 0.97 mmol) was dissolved into 8 mL of THF and 5.0 mL of 1 *N* NaOH (aq.) and stirred for 4 h at reflux. The mixture was diluted with toluene and washed several times with water, dried over  $Na_2SO_4$ , filtered and concentrated. 0.29 g (63%) of **18** were obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.18 (d, J = 8.5 Hz, 2H, biphenyl), 8.08 (d, J = 8.5 Hz, 2H, ArH), 7.72 (d, 2H, biphenyl), 7.59 (d, J = 8.8 Hz, 2H, biphenyl), 7.55 (d, 2H, ArH), 7.00 (d, 2H, biphenyl), 4.03 (t, J = 6.5 Hz, 2H,  $CH_2OAr$ ), 3.68 (t, J = 6.5 Hz, 2H,  $CH_2OH$ ), 1.84 (m, 2H, alkyl chain), 1.63 (m, 2H, alkyl chain), 1.53 (m, 2H, alkyl chain), 1.47 (m, 2H, alkyl chain), 1.38 (s, 9H,  $CH_3$ ). Anal. calcd. for  $C_{30}H_{34}N_2O_3$  ( $M_w$  470.60 g mol<sup>-1</sup>): C 76.57, H 7.28, N 5.95; found: C 76.72, H 7.22, N 5.98.

## 2-(4-tert-Butylphenyl)-5-(4'-(6-(4-vinylbenzyloxy)hexyloxy) biphenyl-4-yl)-1,3,4-oxadiazole (19)

**18** (1.10 g; 2.34 mmol) and Na (54 mg; 2.34 mmol) were placed into a round-bottom flask with septum. The apparatus was evacuated and flushed with Ar several times. 3 mL of THF abs. were added and the mixture was stirred at 60 °C for 18 h until the Na was solved and a white precipitation was formed. A solution of 1-(Chloromethyl)-4-vinylbenzene (1.16 g; 7.60 mmol, technical, purified before with silica gel 60) in 3 mL of THF was injected drop wise. The solution was stirred for 2 h at 60 °C, diluted with diethyl ether, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. After crystallization from EtOH 0.34 g (25%) of **19** were obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.18 (d, J = 8.5 Hz, 2H, biphenyl), 8.09 (d, J = 8.8 Hz, 2H, ArH), 7.72 (d, 2H, biphenyl), 7.59 (d, J = 8.8 Hz, 2H, biphenyl), 7.57 (d, 2H, ArH), 7.39 (d, J = 8.2 Hz, 2H, ArH), 7.30 (d, 2H, ArH), 7.00 (d, 2H, biphenyl), 6.71 (dd, J = 11.0 Hz, 17.6 Hz, 1H, CHCH<sub>2</sub>), 5.74 (d, 1H, CHCH<sub>2</sub>), 5.23 (d, 1H, CHCH<sub>2</sub>), 4.50 (s, 2H, ArCH<sub>2</sub>O), 4.02 (t, J = 6.6 Hz, 2H, CH<sub>2</sub>OAr), 3.49 (t, J =6.6 Hz, 2H, ArCH<sub>2</sub>OCH<sub>2</sub>), 1.83 (m, 2H, alkyl chain), 1.67 (m, 2H, alkyl chain), 1.49 (m, 4H, alkyl chain), 1.38 (s, 9H, CH<sub>3</sub>). Anal. calcd. for C<sub>39</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub> ( $M_w$  586.76 g mol<sup>-1</sup>): C 79.83, H 7.21, N 4.77; found: C 79.69, H 7.20, N 4.71.

### 2-(benzo[b]thiophen-2-yl)pyridine (btp)

In a round-bottom flask with septum 2-bromopyridine (1.00 g; 5.60 mmol) and Tetrakis(triphenylphosphine)palladium (0) ( $1.50 \times 10^{-3}$  g; 0.013 mmol) were weighed and the apparatus was evacuated and flushed with Ar three times. 30 mL of dry THF, thianaphthen-2-boronic acid (0.98 g; 6.18 mmol) and 20 mL 1 *N* Na<sub>2</sub>CO<sub>3</sub> (aq.) were added. The mix-

ture was stirred at 60 °C over night. The reaction mixture was allowed to cool to room temperature and poured into 200 mL of water. The precipitate was filtered, solved in CHCl<sub>3</sub>, washed twice with water, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated. Column chromatography with CHCl<sub>3</sub> gave the pure product (0.92 g, 78%) as white crystals.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.64 (m, 1H, pyridyl), 7.88 (m, 1H, benzthienyl), 7.84 (s, 1H, benzthienyl), 7.81 (m, 2H, pyridyl), 7.73 (m, 1H, benzthienyl), 7.36 (m, 2H, benzthienyl), 7.21 (m, 1H, pyridyl). Anal. calcd. for  $C_{13}H_9NS$  ( $M_w$  211.28 g mol<sup>-1</sup>): C 73.90, H 4.29, N 6.63, S 15.18; found: C 74.06, H 4.83, N 6.40, S 14.46.

### 2-(2,4-difluorophenyl)pyridine (F2ppy)

Using the same procedure like **btp**, 2-bromopyridine (1.00 g; 6.34 mmol) and 2,4-difluorophenyl boronic acid (1.10 g; 6.97 mmol) lead to the pure product **F2ppy** (2.93 g, 80%) as white crystals.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.71 (m, 1H, pyridyl), 8.00 (m, 1H, Ar), 7.74 (m, 2H, pyridyl), 7.24 (m, 1H, pyridyl), 7.00 (m, 1H, Ar), 6.91 (m, 1H, Ar). Anal. calcd. for C<sub>11</sub>H<sub>7</sub>F<sub>2</sub>N ( $M_w$  191.18 g mol<sup>-1</sup>): C 69.11, H 3.69, N 7.33; found: C 69.00, H 3.66, N 7.31.

#### 6-(4-Vinylphenyl)-hexan-2,4-dion (ket)

In a round-bottom flask with septum sodium hydride (1.97 g; 82.1 mmol) was weighed and the apparatus was evacuated and flushed with Ar three times. 100 mL THF abs. and hexamethylphosphamide (1.6 mL; 9.17 mmol) were added and cooled to 0 °C. Acetyl acetonate (4.00 g; 40.0 mmol) was injected while foaming and a white precipitation could be observed. The mixture stirred for 20 min at 0 °C. n-BuLi (1.6 M in hexane, 28 mL; 44.8 mmol) was slowly added and the mixture stirred for another 20 min. 1-(Chloromethyl)-4vinylbenzene (6.41 g; 42.0 mmol, technical, purified before with silica gel 60) was injected drop wise and the mixture was allowed to stir 20 min at RT. To get rid of spare sodium hydride, 2 N HCl was added slowly until no further gasification could be observed. The reaction mixture was diluted with diethyl ether and washed several times with water, dried with Na2SO4, filtered and concentrated. Column chromatography with hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1 lead to the pure product (6.80 g; 79%) as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): keto (15%): 7.32 (d, J = 8.1, 2H, ArH), 7.14 (d, 2H, ArH), 6.68 (dd, J = 10.7 Hz, 17.6 Hz, 1H, CHCH<sub>2</sub>), 5.71 (d, 1H, CHCH<sub>2</sub>), 5.20 (d, 1H, CHCH<sub>2</sub>), 3.54 (s, 2H, COCH<sub>2</sub>CO), 2.89 (t, 2H, ArCH<sub>2</sub>), 2.82 (t, 2H, COCH<sub>2</sub>), 2.19 (s, 3H, CH<sub>3</sub>). enol (85%): 7.33 (d, J = 8.1 Hz, 2H, ArH), 7.15 (d, 2H, ArH), 6.68 (dd, J = 10.7 Hz, 17.6 Hz, 1H, CHCH<sub>2</sub>), 5.71 (d, 1H, CHCH<sub>2</sub>), 5.47 (s, 1H, COHCHCO), 5.20 (d, 1H, CHCH<sub>2</sub>), 2.92 (t, 2H, CH<sub>2</sub>Ar), 2.58 (t, 2H, COCH<sub>2</sub>), 2.03 (s, 3H, CH<sub>3</sub>). Anal. calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> ( $M_w$  216.28 g mol<sup>-1</sup>): requires C 77.75, H 7.46; found: C 78.04, H 7.63.

## $[{Ir(\mu-Cl)(L)_2}_2]$

L = 2-phenylpyridine (ppy); 2-benzo[b]thiophen-2-yl-pyridine (btp); 2-(2,4-difluorophenyl)-pyridine (F2ppy). [{Ir( $\mu$ -Cl)(coe)\_2] (0.55 mmol) and the corresponding ligand L

(2.20 mmol) were dissolved in 30 mL of toluene under nitrogen atmosphere and refluxed with stirring for 1h. After cooling to room temperature, the precipitate was filtered off, washed twice with 10 mL portions of toluene and dried in vacuum.

**1[{Ir(\mu-CI)(ppy)\_2}\_].** Yield 92%, Anal. calcd. for C<sub>44</sub>H<sub>32</sub>Ir<sub>2</sub>N<sub>4</sub>Cl<sub>2</sub> ( $M_w$  1072.11 g mol<sup>-1</sup>): C 49.29, H 3.01, N 5.23; found: C 49.31, H 3.05, N 5.19.

**2[{Ir(\mu-Cl)(btp)\_2}\_2].** Yield 84%, Anal. calcd. for C<sub>52</sub>H<sub>36</sub>Ir<sub>2</sub>N<sub>4</sub> S<sub>4</sub>Cl<sub>2</sub> ( $M_w$  1300.47 g mol<sup>-1</sup>): C 48.03, H 2.79, N 4.31; found: C 48.08, H 2.73, N 4.29.

**3[{Ir(\mu-Cl)(F2ppy)\_2}\_].** Yield 74%, Anal. calcd. for C<sub>44</sub>H<sub>28</sub> F<sub>8</sub>Ir<sub>2</sub>N<sub>4</sub>Cl<sub>2</sub> ( $M_w$  1220.07 g mol<sup>-1</sup>): C 43.32, H 2.31, N 4.59; found: C 43.35, H 2.30, N 4.54.

#### [Ir(L)<sub>2</sub>(ket)]

L = 2-phenylpyridine (ppy); 2-benzo[b]thiophen-2-yl-pyridine (btp); 2-(2,4-difluorphenyl)-pyridine (F2ppy); ketone = 6-(4-vinyl-phenyl)-hexane-2,4-dione.  $[{Ir(\mu-Cl)(L)_2}_2]$  (0.47 mmol) and silvertrifluoroacetate (208 mg, 0.94 mmol) were dissolved under nitrogen atmosphere in 40 mL of acetone and refluxed with stirring for 1 h. After cooling to room temperature, the precipitated AgCl was filtered off. The ketone (1.00 mmol) and 0.5 mL of NEt<sub>3</sub> were added and the resulting solution was stirred overnight at room temperature whereupon the solvent was evaporated under reduced pressure. The remaining residue was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography on alumina with CH<sub>2</sub>Cl<sub>2</sub> as the eluant. The solvent was reduced to about 3 mL and the compound precipitated by adding hexane (20 mL). The precipitate was filtered off, washed twice with 10 mL portions of hexane, and dried in vacuum.

*TEG* (Yield: 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.47 (d, J = 1Hz, 6 Hz, 1H), 8.21 (d, J = 1Hz, 6 Hz, 1H), 7.80 (t, J = 6 Hz, 2H), 7.66 (m, 2H), 7.53 (t, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 7.09 (m, 1H), 6.94 (m, 1H), 6.89 (d, J = 8 Hz, 2H), 6.80 (m, 2H), 6.69 (m, 3H), 6.28 (dd, J = 8 Hz, 12 Hz, 2H), 5.67, (dd, J = 1 Hz, 18 Hz, 1H), 5.19 (d, J = 10 Hz, 1H), 5.17 (s, 1 Hz). Anal. calcd. for C<sub>36</sub>H<sub>30</sub>IrN<sub>2</sub>O<sub>2</sub> ( $M_w$  714.87 g mol<sup>-1</sup>): C 60.49, H 4.23, N 3.92; found: C 60.25, H 4.31, N 3.89.

*TER* (Yield: 58%). <sup>1</sup>H NMR (270 MHz, Aceton-d<sub>6</sub>,  $\delta$ ): 8.50 (m, 1H), 8.16 (m, 1H), 7.98 (m, 2H), 7.72 (m, 4H), 7.24 (m, 1H), 7.08 (m, 5H), 6.83 (m, 4H), 6.68 (dd, J = 10 Hz, 18 Hz, 1H), 6.25 (m, 2H), 5.71 (dd, J = 1 Hz, 18 Hz, 1H), 5.36 (s, 1H), 5.17 (dd, J = 1 Hz, 11 Hz, 1H), 2.58 (m, 2H), 2.38 (m, 2H), 1.70 (s, 3H). Anal. calcd. for C<sub>40</sub>H<sub>30</sub>IrN<sub>2</sub>O<sub>2</sub> ( $M_w$  827.03 g mol<sup>-1</sup>): C 58.09, H 3.66, N 3.39; found: C 57.98, H 3.55, N 3.28.

*TEB* (Yield: 68%). <sup>1</sup>H NMR (400 MHz, Aceton-d<sub>6</sub>,  $\delta$ ): 8.50 (m, 1H), 8.23 (m, 3H), 8.01 (m, 2H), 7.42 (m, 1H), 7.22 (d, J = 8 Hz, 3H), 6.88 (d, J = 8 Hz, 2H), 6.68 (dd, J = 6.7 Hz, 18 Hz, 1H), 6.46 (m, 2H), 5.72 (dd, J = 1 Hz, 18 Hz, 1H), 5.65 (dd, J = 4Hz, 8 Hz, 2H), 5.32 (s, 1H), 5.16 (dd, J = 1 Hz, 11 Hz, 1H), 2.62 (m, 2H), 2.45 (m, 1H), 2.32 (m, 1H), 1.69 (s, 3H). Anal. calcd. for C<sub>36</sub>H<sub>26</sub>IrF<sub>4</sub>N<sub>2</sub>O<sub>2</sub> ( $M_w$  786.83 g mol<sup>-1</sup>): C 54.95, H 3.33, N 3.56; found: C 54.79, H 3.37, N 3.60.

#### **Polymerization Conditions**

All polymers described were synthesized by means of a free radical process. The monomer concentration of each reaction was 100 g L<sup>-1</sup> in freshly distilled THF and 2 mol % *N*,*N*-azobisisobutyronitrile (AIBN) was chosen as initiator. All reactions were carried out in a glove box system at 50 °C for 72 h. The resulting solutions were allowed to cool to room temperature and purified by repeated precipitation into 120 mL of MeOH/diethyl ether 2:1. The polymers were solved again in THF and filtered through a syringe PTFE filter 0.2  $\mu$ m. The solvent was removed in vacuum and the solutions precipitated again into 120 mL MeOH/diethyl ether 2:1. The residues were filtered by the use of PTFE filters pore size 0.45  $\mu$ m and dried for 30 h at 80 °C in vacuum.

#### **RESULTS AND DISCUSSION**

In this article, we report on influences of alkyl spacer lengths between a polystyrene backbone and electron-transporting respectively hole-transporting units attached with and without a hexyl-spacer at the "para" position of each styrene monomer. The kind of linkage of active side groups to the inert polystyrene backbone, especially the spacer length between the side group and the polystyrene main chain, seems to be important for the material's electronic properties. To verify this influence, the active side groups were connected via hexyl spacers on one hand, and without these spacers directly to the polymeric backbone on the other hand. In the following, the syntheses of functionalized styrene monomers and of the resulting different copolymers are presented. One layer PLEDs with very simple hole- and electron-transporting molecules were utilized to study the emission properties of these materials. As hole-transporting material N,N-Di-p-tolyl-aniline and as electron-transporting 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole unit (tert-BuPBD) were established.

#### **Synthesis**

#### **Monomer Syntheses**

**Hole-Transporting Monomers.** A convenient way to introduce a vinyl group into very basic triarylamines is to utilize N,N-Bis(4-methylphenyl)-aminobenzaldehyde **1** as educt. Wittig-reaction with *in situ* prepared phosphonium ylide of methyl triphenyl phosphonium bromide and butyl lithium lead directly to the vinyl functionalized hole-transporting monomer **2** (Scheme 1). For the introduction of a hexyl-spacer group, 4-Bromo-N,N-di-p-tolylaniline **3** was selected



**SCHEME 1** Synthesis of the hole-transporting monomer **2** without spacer.



SCHEME 2 Reaction scheme for the hole-transporting monomer 6 with hexyl spacer.

as starting material (Scheme 2). Dehalogenation with *n*-Butyl lithium, followed by the addition of pyrane protected 6-Bromohexanol **4**, lead to an intermediate, unprotected easy by the use of 2 *N* hydrochloric acid to generate the free alcohol **5**. The last step could be done by a Williamson ether synthesis of 1-chloromethyl-4-vinyl-benzene with the *in situ* prepared sodium-alcoholate of **5** to obtain the vinyl functionalized monomer **6**.

Electron-Transporting Monomers. The synthesis of vinyl functionalized tert-BuPBD is shown in Scheme 3, and was done in accordance to Boiteau et al.<sup>21</sup> The introduction of the hexyl-spacer group into tert-BuPBD turned out to be a little more difficult compared to the hole-transporting material. Direct insertion of the spacer moiety into tert-BuPBD was discovered during the first attempts to be unpractical. Therefore, the final seven step reaction scheme, shown in Scheme 4, was established. Starting material is 4'-Hydroxybiphenyl-4-carboxylic acid **11** and the first step was a sulphuric acid catalyzed esterification with ethanol. The protected ethyl ester compound **12** was functionalized with the  $C_6$ -spacer group, using 6-Bromohexanol as reagent. In a further step, hydrazine hydrate leads to the carbonyl hydrazide derivative 14 in a good yield. By a following amidation with 4-tert-Butylbenzoyl chloride 15 the dicarbonyl hydrazide derivative 16 was obtained. Final dehydration cyclization leads to the 1,3,4-oxadiazole derivative 17. After an alkaline saponification of the ethyl ester and final Williamson ether synthesis of the alcohol with sodium and 1-(Chloromethyl)-4-vinylbenzene, the monomer 19 with a styrene-functionality was obtained.

**Emitting Materials.** To introduce polymerisable functional groups into iridium-(III) complexes with chromophoric ligands, it was necessary to vinylise the saturation ligand, which reacts with the dichloro diiridium intermediate in the last step of each reaction sequence. An acetylacetonate derivative with a styrene moiety was used. The triplet emitting complex was achieved for green (**TEG**), red-orange (**TER**), and bluish-green (**TEB**) with color endowing ligands ppy for **TEG**, btp for **TER** and 2-(2,4-difluorophenyl)pyridine (F2ppy) for **TEB** (Fig. 1).

#### **Polymerization**

Combining the synthesized styrene monomers seven copolymers 20-26 were obtained with hexyl spacer, without spacer, and in different emitting colors (Fig. 2). Polymer 20 consists of both spacer functionalized transporting monomers 6 and 19. Polymer 21, 22, and 23 consisted of the untethered electron-transporting material 9 and the hole-transporting material 6 with spacer unit, whereas polymers 24, 25, and 26 only exhibited the two un-tethered monomers 2 and 9. Free radical polymerisations of the styrene monomer mixtures were carried out using azobisisobutyronitrile (AIBN) as initiator and tetrahydrofuran as solvent. All synthesized polymers were obtained in acceptable yields of  $\sim$ 70%. The ratio of transporting monomers was selected with 2:1 electron to hole transporting monomer in each polymerization reaction. This ratio was discovered to perform the best results in PLEDs by preliminary experiments using blend systems of active molecules in a polystyrene matrix. The ratio of the hole- respectively electron-transporting



**SCHEME 3** Synthesis of the electron-transporting monomer **9** without spacer.

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SCHEME 4 Reaction scheme for the electron-transporting monomer 19 with a hexyl spacer.

component was estimated with <sup>1</sup>H NMR spectroscopy. As listed in Table 1, the selected monomer ratio could only be obtained in copolymers consisting of structural equal monomer types. For polymer **20**, with two of the monomers tethered to the polystyrene backbone via hexyl spacers, the ratio could be achieved as selected before. For polymers **22** and **23**, with hexyl-spacer connected hole-transporting monomers, it was shown that the monomer with spacer functionality is enriched. Finally, polymers **25** and **26** featured again the selected ratio of the un-tethered monomers. Hence it could be concluded that monomers carrying a hexyl spacer exhibited higher polymerization rates compared to those without. This may be caused by different solubilities generated mainly by the hexyl spacer moieties.

The triplet emitting monomer ratio was selected with 7.4 wt % with respect to the transporting monomer mixture. The molar ratio of the iridium complex in all synthesized copolymers could not be identified by NMR spectroscopy because of its small amount and because of very broad polymer signals overlapping the emitter signals. Therefore, an acidic pulping of the polymer in concentrated nitric acid and concentrated perchloric acid under microwave irradiation had to be done, before the Ir-content could be measured on ICP-OES. In Table 1 it is noticed that the iridium content varies of about 30% in the obtained polymers to the preselected amount. It could be concluded that the content of the iridium complex is about 90% of the selected monomer ratio in copolymers, whenever a tethered monomer is present (poly-

mers 20–23). With two un-tethered monomers, see copolymers 24–26, the content of the phosphorescent dopand decreased to ~70% of the preselected amount. The numberaverage molecular weights of all polymers of ~25 kg mol<sup>-1</sup> determined by size exclusion chromatography were sufficient to perform good film-building properties. Polydispersities of about 2, in the case when hexyl spacers were present for copolymers 20–23, are quite normal for free radical polymerisations. Copolymers 24–26, without any spacer, exhibited a little higher value of about 2.5, what may be caused by a lower solubility of these materials. Furthermore, it could be expected that glass transition temperatures depend on the introduced spacer length. In Table 1 the limitation of  $T_{\rm g}$  to 78 °C is listed for polymer 20 with the two tethered monomers. In the case when only one charge transport



FIGURE 1 Structure of the different styrene-functionalized Ircomplexes TEG, TER, and TEB used as emitting materials.



FIGURE 2 Chemical structure of the investigated copolymers 20-26.

monomer carries a hexyl spacer, an increasing of glass transition temperatures to about 125–140 °C in polymers **21–23** could be observed. Polymers **24–26** showed enhanced glass transition temperatures of nearly 200 °C. This drastically increase of the glass transition temperature can be explained by the bulky side groups, directly linked to the polystyrene backbone. They involved an extension of the polystyrene main chain and thereby a decrease of their movability, compared to un-substituted polystyrene ( $T_{\rm g} = 105$  °C).

## UV/Vis- and Photoluminescence Spectroscopy

UV/Vis spectra of the three green emitting polymer films of 20, 21, and 24 are plotted in Figure 3(a). It was shown that absorbance maxima of all polymers (open symbols) were in the range of about 307 nm, which indicated spin-allowed  $^{1}\pi$ - $\pi^*$  interligand transitions of the emitter between 200 and 340 nm on the one hand and the absorbance maximum of the polymer matrix with *tert*-BuPBD and *N*,*N*-Di-p-tolyl-aniline at 307 nm<sup>22</sup> on the other hand. Whereas, the spinallowed metal to ligand charge transfer (<sup>1</sup>MLCT) could be ascribed between 350 and 450 nm. The spin-forbidden  ${}^{3}\pi$ - $\pi^{*}$ and <sup>3</sup>MLCT could be anticipated from 450 to 550 nm.<sup>23</sup> An excitation wavelength of 465 nm was selected for photoluminescence spectra, shown in Figure 3(a) (full symbols). The emission maxima were ascertained at about 530 nm for all green emitting polymers, while the Ir(ppy)<sub>2</sub>acac triplet emitter itself shows an emission maximum at 516 nm in 2-methyltetrahydrofuran solution.24

Figure 3(b) shows the UV/vis behavior of the red triplet emitting polymer films of **22** and **25**. Absorbance maxima at

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around 307 nm could be mainly related to the transporting polymer matrix, as well. <sup>1</sup>MLCT and <sup>3</sup>MLCT bands were, in accordance with the literature, observed in the range of 400–500 nm.<sup>25</sup> For photoluminescence spectra (full symbols) plotted in Figure 3(b) an excitation wavelength of 495 nm was selected. The emission maxima of the red emitting polymer systems were ascertained at about 620 nm which could be assigned to electronic origin transitions broadened inhomogeneously and electron-phonon coupling. Furthermore they exhibited an additional shoulder at around 665 nm and above which depicts overlapping vibrational satellites, while the Ir(btp)<sub>2</sub>acac emitter itself shows an emission maximum at 612 nm in 2-methyltetrahydrofuran solution.<sup>26</sup>

UV/Vis and photoluminescence behavior of polymers 23 and 26 are shown in Figure 3(c) and summarized in Table 2. Maxima of absorbance (open symbols) were with 307 nm in the same range as the absorbance maxima of the green respectively red emitting polymers and could be mainly regarded to the polymeric matrix system. The excitation wavelength for photoluminescence spectra (full symbols) was 307 nm for both polymer films. The un-tethered blue emitting polymer 26 showed an emission maximum at 493 nm. Especially remarkable is the 10 nm bathochromic shift between the maxima of the tethered polymer 23 and the untethered polymer 26 but the origin of this phenomenon is unknown recently. A slight shoulder at 457 nm was observed for both polymers and showed an increased emission in the un-tethered case. Compared with literature,<sup>27</sup> the maximum of absorbance of the Ir(F2ppy)2acac triplet emitter itself

Copolymer		20	21	22	23	24	25	26
Approximate yield in %		66	69	67	74	78	73	71
Elemental analysis in %	С	79.04 (80.03)	80.59 (81.83)	80.63 (81.68)	80.32 (81.44)	81.42 (82.23)	81.58 (81.94)	81.79 (81.75)
(expected from monomer ratio)	Н	7.08 (7.23)	6.68 (6.82)	6.78 (6.73)	6.73 (6.70)	6.32 (6.41)	6.18 (6.32)	6.20 (6.28)
	Ν	4.18 (4.19)	5.68 (5.47)	5.51 (5.54)	5.44 (5.45)	6.50 (6.42)	6.48 (6.37)	6.49 (6.39)
Ir analysis in % (expected from monomer ratio)	lr	1.69 (1.99)	1.76 (1.99)	1.60 (1.73)	1.63 (1.82)	1.22 (1.98)	1.20 (1.72)	1.24 (1.78)
Selected molar monomer ratio	х	0.628	0.637	0.640	0.639	0.642	0.645	0.644
	У	0.314	0.319	0.321	0.320	0.321	0.322	0.322
	z	0.058	0.044	0.039	0.041	0.037	0.033	0.034
Molar copolymer composition (x, y calcd. from <sup>1</sup> H NMR integrals) (z calcd. from Ir analysis)	х	0.63	0.62	0.56	0.54	0.72	0.67	0.67
	У	0.37	0.38	0.44	0.46	0.28	0.33	0.33
	z	0.049	0.043	0.036	0.036	0.023	0.023	0.021
GPC in 10 <sup>3</sup> g mol <sup>-1</sup>	<i>M</i> <sub>n</sub>	22.9	27.2	29.6	26.8	22.3	33.9	28.2
	$M_{\rm w}$	40.9	57.6	60.7	55.5	61.3	74.7	67.8
	PDI	1.79	2.12	2.05	2.07	2.75	2.50	2.41
DSC in °C	Tg	78	140	137	125	194	196	197

**TABLE 1** Overview on Selected Monomer Ratios, Obtained Copolymer Composition, Molecular Weight and Glass Transition Temperatures ( $T_g$ ) of the Terpolymers **20–26** 

should be at 476 nm, measured in chloroform solution. There is an overall adjustment of more than 25 nm observable for both polymer systems, while the adjustment is maximized when a tethered hole transporting monomer is used.

#### **Cyclovoltammetric Investigations**

For nonconjugated polymer backbones carrying the active molecules as side-chains, hopping processes between these

side moieties are the main charge transport mechanism, in contrast to conjugated polymers, where transport along the polymer backbone is a basic mechanism. In our case, organic  $\pi$ -conjugation of the attached charge transport materials provides redox-isolated sites and/or charge hopping sites for electrons and permits intermolecular electron transfer processes, therefore. Cyclic voltammetry (CV) is one suitable possibility to investigate electronic properties in the solid state



FIGURE 3 UV/Vis- and photoluminescence spectra (a) of the green emitting polymers 20, 21, and 24 (with TEG) as solid films (open symbols absorbance, full symbols photoluminescence). (b) Of the red emitting polymers 22 and 25 (with TER) as solid films (open symbols absorbance, full symbols photoluminescence). (c) Of the blue emitting polymers 23 and 26 (with TEB) as solid films (open symbols absorbance, full symbols photoluminescence).

Copolymer	20	21	22	23	24	25	26
Onset voltage in V	4.4	2.9	3.2	3.5	2.4	2.5	2.6
Brightness in cd m <sup>-2</sup> @ 8 V	40	2,250	450	160	3,200	700	400
Luminous efficiency in cd A <sup>-1</sup> @ 6 V	1.8	15.7	2.6	1.9	27.7	4.9	4.3
Electroluminescence maxima in nm	523	523	615	507	521	615	498
Absorbtion maxima as film in nm	310	309	308	307	306	307	308
Photoluminescence maxima as film in nm	532	526	621	493	529	616	483

TABLE 2 phPLED, UV/vis and Photoluminescence Data of the Terpolymers 20-26

and to get an idea of the electrochemical redox behavior. Additionally, it is possible to estimate HOMO- and LUMOenergy levels from CV measurements. Consequently, we used this method to extract information about the electron transfer activities of our synthesized polymer materials as electroactive films, deposited on a glassy carbon working electrode. 0.1 *M* tetrabutylammonium tetrafluoroborate ( $Bu_4NBF_4$ ) in acetonitrile was used as electrolyte, besides a platinum mesh as counter electrode and an Ag/AgCl-electrode as reference.

Reversible reduction processes were detected in the cathodic sweep direction at very negative values for polymers 20, 21 and 24 [Fig. 4(a)]. The identified reduction peak potentials were in the range from -2.10 V to -2.19 V and the corresponding re-reduction peaks at -1.95 V. This electrochemical redox behavior could be attributed to the tert-BuPBD units attached as side groups to the polystyrene backbone. In solution tert-BuPBD 7 exhibits a reversible reduction step with a peak potential at -1.96 V,<sup>28</sup> whereas the polymer films exhibited a 150 mV shift to more negative values, allegeable by the diffusion of counter ions into the polymer film to maintain charge neutrality. In the oxidation direction only quasi-reversible oxidation steps were observed, assigned mainly to the hole-transporting units in the polymer structure [Fig. 4(a)]. The oxidation peaks of the polymer films were located at +0.98 V  $\pm$  20 mV and the corresponding cathodic peaks could be found at +0.90 V. In solution the N,N-Di-p-tolyl-aniline molecule shows also a reversible oxidation

step at around +0.90 V.29 The oxidation processes of the polymers were more or less not of complete reversibility, since additional hole transfers from the hole transporting material to TEG are imaginable. Measured in solution, TEG exhibited a reversible and a second quasi-reversible oxidation step [Fig. 4(b)]. The ascertained half wave potential of the first oxidation step was at  $E_{1/2}$ : +0.87 V, whereby the electrochemical activity of TEG was in the same range as that one of the hole transport material. The assumption, that the possible hole transfer from the N,N-Di-p-tolyl-aniline side group to TEG is reasonable for noncomplete reversible oxidation processes of the terpolymers, is supported by the oxidation behavior of the corresponding copolymers without TEG. Only copolymers without an attached emitter showed good reversibility.<sup>30</sup> The electrochemical behavior seemed to be finally independent from the spacer length between the polymer backbone and the attached active molecules. The electrochemical redox performance was defined by introduced  $\pi$ -conjugated hole- and electron-transporting molecules and Ir-complexes connected to the polymer backbone. It was shown that in all cases intermolecular charge transfer is possible through hopping processes between the attached charge transport materials. This is an important requirement for the electronic application for these polymers in PLEDs.

#### **Device Characterization**

For all obtained terpolymers **20–26**, phosphorescent PLEDs were built in similar configuration (glass/ITO/PEDOT:PSS/



**FIGURE 4** Cyclic voltammograms (a) of green emitting polymers **20**, **21**, and **24** as film on a glassy carbon electrode (0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile, scan rates 20 mV s<sup>-1</sup>). (b) Of **TEG** in solution (0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile, scan rate 100 mV s<sup>-1</sup>).



FIGURE 5 Device characteristics (a) of the green emitting polymers 20, 21 and 24 (with TEG; full symbols brightness; open symbols luminous efficiency; layer thicknesses about 80 nm). (b) Of the red emitting polymers 22 and 25 (with TER; full symbols brightness; open symbols luminous efficiency; layer thicknesses about 60 nm). (c) Of the blue emitting polymers 23 and 26 (with TEB; full symbols brightness; open symbols luminous efficiency; layer thicknesses about 75 nm).

terpolymer/CsF/Ca/Ag) to compare their electronic properties with respect to the spacer length and the emission colors. For the prepared green emitting polymers the results are shown in Figure 5(a) and Table 2 for polymer layer thicknesses of about 80 nm. The onset voltage of polymer 20 was with 4.4 V considerably higher compared to that of polymers with just one 21 (2.9 V) or respectively none 24 (2.4 V) spacer attached transport monomer. The best overall performance of the green emitting polymers was presented by polymer 24 with nontethered units, showing a brightness of 4500 cd m<sup>-2</sup> at 8.5 V, a luminous efficiency of 28 cd A<sup>-1</sup> at 6 V and the low mentioned onset voltage of 2.4 V. Polymer 20, where both transporting monomers were connected via hexyl spacer groups to the polymer backbone, presented the worst performance. In Figure 6 the electroluminescence spectra of the green emitting PLEDs of polymer 21 and 24 are plotted (open and filled triangles). For these two green emitting materials, the electroluminescence emission maxima were identical at 523 nm and independent from spacer length, therefore. There was also a good accordance to the photoluminescence spectra [Fig. 3(a)]. A similar influence on the emission behavior could be noted for the red-emitting polymers as well, illustrated in Figure 5(b) and Table 2. For the red-emitting polymer 22, consisting of the tethered holetransporting monomer, a brightness of 500 cd  $m^{-2}$  at 8 V with a maximum luminous efficiency of 2.5 cd  $A^{-1}$  at 5 V was observed. The onset voltage of polymer 22 with 3.2 V was, compared to the un-tethered polymer 25 with 2.5 V, substantially higher and showed a similar behavior-comparing the green emitting case. Polymer 25, contained of directly connected transporting units, exhibited, with a brightness of 700 cd  $m^{-2}$  at 8 V and a luminous efficiency of 4.9 cd  $A^{-1}$  at 5 V, a remarkable increase in contrast to the performance of the tethered polymer 22. Therefore, the best overall performance of the investigated red-emitting polymers is presented by polymer 25 without the spacer groups. The electroluminescence spectra of the red-emitting materials are plotted in Figure 6 (open and filled circles). Both

ima at 665 nm and a good accordance to the photoluminescence behavior measured in solid films. With respect to the blue emitting polymers **23** and **26** an analog behavior concerning the green and red-emitting polymers was noticed [Fig. 5(c) and Table 2]. The luminous efficiency for polymer system **23**, containing hexyl-spacer units to fix the holetransporters, was limited to 1.9 cd  $A^{-1}$  at 6 V with a brightness of 300 cd m<sup>-2</sup> at 10 V and an onset voltage of about 3.5 V. With a maximum luminous efficiency of 4.3 cd  $A^{-1}$  at 6 V, a brightness of 800 cd m<sup>-2</sup> at 10 V, and an onset voltage of about 2.7 V, the performance of polymer **26** with untethered transporting units was significantly increased as well as for the other colors. The electroluminescence plot of

curves showed emission maxima at 615 nm and local max-



FIGURE 6 Electroluminescence spectra of the investigated PLEDs (full symbols tethered hole-transporting component, open symbols nontethered components; triangles polymers with TEG, circles polymers with TER and squares polymers with TEB).

polymer 23 and 26 is shown in Figure 6 (open and filled squares). Polymer 26, with the un-tethered monomers, showed with a maximum at 496 nm the behavior expected from photoluminescence experiments. For polymer 23, consisting of the tethered hole-transporting component, two maxima could be observed: one at the expected 503 nm and an additional unexpected local maximum at 583 nm. The origin of this additional emission peak in the electroluminescence spectra is recently unknown and will be investigated in further studies. Furthermore, it has to be noticed, that the choice of device characteristics was done exclusively with respect to comparable layer thicknesses, that is not the best gainable performance for the selected device adjustment was listed finally. It shows only a comparison of polymers, with and without spacer units between the polymer main chain and the connected charge transport materials, and does not illustrate the maximum accessible luminous efficiencies or brightnesses of these materials.

In summary, the experiment has proven that a hexyl spacer unit exhibits a disadvantageous influence regarding all the determined PLED characteristics for the investigated colors. The onset voltage of the phPLED increases on one hand, while the luminous efficiency and the brightness decrease in all cases on the other hand with an application of spacer groups. A possible explanation for this phenomenon could be that the introduction of hexyl-spacers between the transporting units and the polymer main chain, resulting in a drastic decrease of the glass transition temperature, and therefore, allows an unfavorable steric order.

It is imaginable, that the nonconjugated hexyl spacer units of the charge carrier molecules linked to the polymer main chain forming a tube-like nonconductive shield around the emitter, because the emitter itself is connected in a shorter distance to the nonconjugated polymer backbone. In polymer **20** for example, the distance between the electron- and holetransporting units to the polymer backbone is about 7 Å higher than that one of the phosphorescent dopand to the polymer backbone. As a result of such an emitter-shielding the transfer of the injected charges by hopping processes to the phosphorescent dopand becomes more inefficient. So the formation of excitons at the phosphorescent dopand will be reduced and a nonemissive charge recombination becomes more important. This leads to a more inefficient device in the case of the thetered copolymers.

Another possible declaration causing the inefficient PLED performances of the tethered polymers can be that the amount of nonactive parts of the polymer, showing neither emission behavior nor adopting any charge transport tasks, are increased by the use of spacer groups. The semiconductive ratio of the un-tethered polymers is maximized without the use of spacers, therefore. For example, if an imagined copolymer of the tethered electron- and hole-transporting styrene monomers in the ratio 2:1 is at hand, the nonconductive ratio of the polymer with spacers (monomers **19** and **6**) is with 40% very high. Whereas, in the case of just one spacer at the hole-transporting monomer the nonconductive ratio of the copolymer is calculated to 20% and it comes to

a lesser extend with no spacer at both charge carrier moieties. That polymer (monomers **10** and **2**) exhibits a minimized nonconductive ratio of about 8% and should be the best material for efficient charge carrier transportation of that array. This statement is further based on the currentvoltage-characteristics of these materials. Polymer **20** with the two tethered charge carrier moieties shows a current density of only 0.65 mA cm<sup>-2</sup> at 8 V, whereas polymer **24** with no spacer groups shows at 8 V a current density of 11.6 mA cm<sup>-2</sup>. This drastic increase of current density means that much more charge carriers can be injected into the solid film to form excitons for efficient light emission.

Overall it can be summarized, that this established approach of a direct linkage of active components as side functionalities is favorable for polymers with a nonconjugated backbone and their potential for efficient charge transport processes. It is shown that spacer moieties may affect the efficient charge carrier transport from the transporting materials to the phosphorescent dopand in two ways. The first is the maximization of the nonconductive ratio in the nonconjugated polymer and, the second is the possibility of a formation of a nonconductive shield around the phosphorescent dopand, caused by the nonconductive spacer moieties. In further experiments it was established that a white light emitting phosphorescent PLED should be possible with these polymers because of their suppressing undesired energy transfer from the blue to the red emitter in multi component copolymers.<sup>31</sup>

### CONCLUSION

It was possible to synthesize copolymers with hole- and electron-transporting components and additional phosphorescent triplet emitters with and without spacer moieties. The investigation of the resulting polymerization products leads to the prediction that spacer-functionalized monomers exhibit higher polymerization rates. Further, the introduction of spacer moieties has no influence on the electrochemical behavior of the polymers, as shown by CV measurements. Additionally, it was found that an introduction of hexyl-spacer tethered transporting monomers into polymers has a crucial influence on their PLED properties. The glass transition temperatures of polymers containing tethered components are much lower, in contrast to those without the latter. Luminous efficiencies, turnon voltages, and brightnesses were also influenced and restricted by the introduction of spacer units. It was emphasized that transporting materials which are directly connected to the polymer main chain, exhibited the best PLED performance. An explanation for this phenomenon was given by a more efficient charge transport because of a higher content of semiconducting molecules in the copolymer, by a more efficient charge transfer to the phosphorescent dopand and a more efficient exciton formation in the case of the spacerless copolymers. Therefore, the preferred approach for further investigations, based on this study, is the direct linkage of the active molecules without the use of spacer moieties onto the polymer backbone of polystyrene.

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