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A High Molecular Weight Aromatic PhOLED Matrix Polymer Obtained by Metal-Free, Superacid-Catalyzed Polyhydroxyalkylation

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Introduction. The discovery of organic electroluminescent materials (EL) has generated tremendous research efforts toward design and fabrication of efficient organic light-emitting diodes (OLEDs).[1] Poly(9,9-dialkylfluorene-2,7-diyl)s and a series of related copolymers obtained by palladium(0)- or nickel(0)-catalyzed aryl−aryl polycondensation schemes have attracted enormous attention in the past two decades as efficient light emitters or OLED matrix materials in combination with electrophosphorescent dopants.[2] However, degradation studies on polyfluorene-based OLED devices have shown the occurrence of structural defects (“keto” defects) under device operation.[2,3] In addition, residual covalently bound transition metal impurities can cause detrimental effects on the OLED device performance.[4]

In the design of organic emitter or matrix (co)polymers the use of fluorinated aromatic segments can decrease the aggregation tendency and prevent excimer formation, thus resulting in increased electroluminescence (EL) efficiency at reduced turn-on voltages.[5] On the basis of these results, we have designed a first novel and high-molecular-weight aromatic polymer that is obtained in a metal-free, superacid-catalyzed polyhydroxyalkylation after Friedel−Crafts. The aromatic target polymer contains 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,4,5-tetrafluorobenzene structural units as most extended conjugated building blocks in its nonconjugated backbone. According to the superelectrophilicity concept of Olah et al.[6] and our previous work in the synthesis of condensation polymers in superacidic media,[7] we could expect that the two para hydrogens at the 9,9-dimethylfluorene terminals of the bifunctional 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,4,5-tetrafluorobenzene monomer could be condensed with *N*-methylisatin as electrophile in trifluoromethanesulfonic acid (TFSA) to give a high molecular weight polymer.

Here, we would like to report monomer and polymer synthesis, polymer characterization including its optical and electronic properties, and the application of the aromatic high-bandgap polymer with rather high triplet energy as matrix material of phosphorescent OLEDs (PhoLEDs).[8,9]

Experimental Section. *General Methods*. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. ^{1}H and ^{13}C NMR data were obtained on a Bruker ARX 400 spectrometer. Chemical shifts are given in parts per million (ppm) using residual solvent protons as internal standards. Splitting patterns are designated as “s” (singlet), “d” (doublet), “t” (triplet), and “m” (multiplet). Low-resolution mass spectra were obtained on a Varian MAT 311A operating at 70 eV (electron impact, EI) and reported as m/z and percent relative intensity. FD masses were obtained on a ZAB 2-SE-FDP. Elemental analyses were performed at the University of Wuppertal, Department of Analytical Chemistry, using a Perkin-Elmer 240 B. The inherent viscosities of 0.2% (w/w) polymer solutions in 1-methyl-2-pyrrolidinone (NMP) were measured at 25 °C using an Ubbelohde viscometer. Molecular weights were determined by gel permeation chromatography (GPC). The chromatography system was equipped with three Waters styragel columns at 40 °C with THF as the solvent at a flow rate of 1.0 mL/min. The SEC-MALS measurements were performed at 25 °C using a separation system comprising two size-exclusion columns (a Waters HSPgel HR MB-L and a HR MB-B) with a molecular weight range from 5×10^2 to 7×10^5 and 1×10^3 to 4×10^6, respectively. The light scattering measurements were carried out on a Dawn Eos multiangle light scattering (MALS) instrument (Wyatt Technology, Santa Barbara, CA). The HOMO level of polymer **3** was measured with help of an AC-2 surface analyzer from Riken Keiki Co. based on the UV photoelectron spectroscopy (UPS) principle.

Optical Spectroscopy. Absorption measurements of solutions in 1 cm quartz cuvettes or thin films spun on quartz disks (typically 100 nm thick polymer films) where measured using a Perkin-Elmer Lambda 19 spectrophotometer. Fluorescence measurements where made using a Jobin-Yvon Fluorolog spectrofluorimeter. Triplet spectroscopy studies where made using our reference system[10] comprising a pulsed Nd:YAG laser (pulse width 120 ps, maximum pulse energy at the excitation wavelength, 355 nm, 7 mJ, repetition rate 1−10 Hz) excitation source. The light emitted by the sample was dispersed using a spectrograph (Jobin-Yvon Triax 190) and subsequently detected by a gated intensified CCD camera (4 Picos, Stanford Computer Optics). “Gated” refers to an adjustable time delay after the trigger pulse (provided by a fast photodiode responding to the excitation laser) set before the start of detection, with the duration of detection also being tunable (the time resolution is limited by a minimum gate width of 200 ps.[11] In order to smooth laser intensity fluctuations, every spectrum (measure point) was

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obtained by accumulating up to 50 laser shots. Measurements are made at low temperature using a helium displex cryostat (frozen solution in the case of solution samples).

PhoLEDs. All organic layers were prepared by spin-coating onto patterned, precleaned, and ozone-treated indium tin oxide (ITO)-coated glass substrates. A hole injecting PEDOT:PSS (Baytron P Al 4083) layer was spin-coated onto the substrates under clean-room conditions yielding layers of 36 nm, which were baked at 110 °C for 2 min to remove residual water. For the further processing steps the substrates were transferred to a nitrogen box. The cross-linkable hole conductor HTL 1 was dissolved in toluene, 2 wt % of the photoinitiator 4-octyloxydiphenyliodonium hexafluoroantimonate (OPPI) was added, and finally the solution was spin-cast on top of the PEDOT:PSS layer. The films were irridiated with UV-light (365 nm wavelength) for 6 s and subsequently cured at 110 °C for 1 min to promote cross-linking. The second hole-transport layer (HTL2) was spun-cast and cross-linked in the same way as the first layer, but contained only 0.5 wt % photoinitiator. The detailed mechanism of the cross-linking reaction as well as the chemical structures of the photoinitiator and the hole conductors are published elsewhere.[12] The matrix polymer **3** (5 mg/mL) and the green emitter were dissolved separately in chloroform and chlorobenzene, respectively, and mixed just prior to spin-coating. The preparation of the emissive layer was completed by a postbaking step at 150 °C for 10 min.

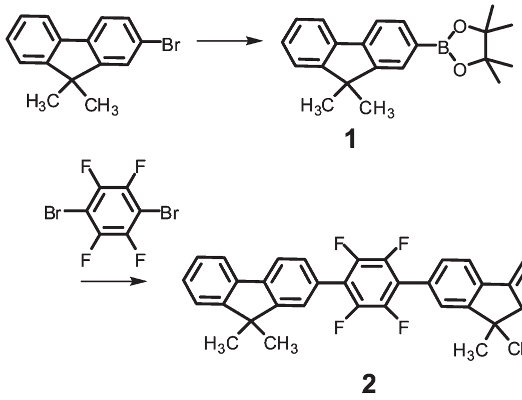
The cathode, consisting of a 2 nm thin layer of CsF and an Al layer (100 nm), was deposited by thermal evaporation at a base pressure of 10^{-6} mbar. The device characterization was done with a Keithley 2400 source meter, a calibrated photodiode, and an Ocean Optics SD2000 CCD spectrometer under an argon atmosphere.

Synthesis of the Monomers

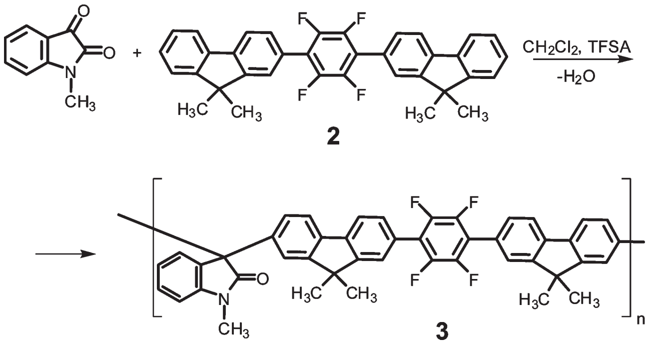
*9,9-Dimethylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**).* At −78 °C a 1.6 M solution of *n*-BuLi in hexane (0.92 g, 14.3 mmol) was added dropwise to a solution of 2-bromo-9,9-dimethylfluorene (3.0 g, 11.0 mmol) in dry THF (40 mL). The mixture was stirred for 1 h at −78 °C. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.66 g, 14.3 mmol) was slowly added and stirred for another 15 min at −78 °C. Afterward, the solution was allowed to return to room temperature and then stirred for 24 h before being poured into water. The aqueous phase was then extracted with dichloromethane, the collected organic layers were dried over $MgSO_4$, and the solvent was removed by rotary evaporation. After recrystallization of the residue from heptane we obtained 2.3 g (65%) of a colorless solid. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 32 °C): 7.82 (s, 1H), 7.75 (dd, 1H), 7.70 (m, 1H), 7.66 (d, 1H), 7.39 (td, 1H), 7.28 (m, 2H), 1.45 (s, 6H), 1.30 ppm (s, 12H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 32 °C): 154.5, 153.0, 142.3, 139.1, 134.1, 129.1, 128.2, 127.2, 123.0, 120.8, 119.6, 84.0, 47.1, 27.4, 25.3 ppm. Anal. Calcd for $C_{21}H_{25}BO_2$: C 78.76; H 7.87. Found: C 78.73; H 8.22. FD-MS: 320 (M^+). Melting point: 133 °C.

*1,4-Bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene (**2**).* 1,4-Dibromo-2,3,5,6-tetrafluorobenzene (1.91 g, 6.24 mmol), 9,9-dimethylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**) (4.00 g, 12.48 mmol), tetrakis(triphenylphosphino)Pd(0) (0.20 g, 0.17 mmol), and solid Na_2CO_3 (6.00 g, 56.6 mmol) were stored in a Schlenk tube. Then, degassed toluene (30 mL), *n*-butanol (24 mL), and water (30 mL) were added, and the mixture was refluxed under argon for 48 h. The reaction was quenched by adding 30 mL of 2 M aqueous HCl, and 50 mL of chloroform was added. The mixture was subsequently washed with concentrated aqueous Na_2CO_3 solution, concentrated titriplex solution, and brine and dried over Na_2SO_4, and the solvent removed by rotary evaporation. The residue was purified by column chromatography over silica gel (hexane/dichloromethane 9:1) to obtain 1.4 g (42%) of a white, glassy solid. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 32 °C): 7.80 (d, 2H), 7.72 (dd, 2H), 7.53 (s, 2H), 7.46 (d, 2H), 7.42 (dd, 2H), 7.32 (dd, 4H), 1.47 ppm (s, 12 H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 32 °C): 154.3, 154.1, 145.6, 143.3, 140.4, 138.6, 129.4, 128.3, 127.5, 126.3, 124.9, 123.1, 120.7, 120.4, 47.3, 27.4 ppm. FD-MS: 534.8 (M^+).

Scheme 1. Monomer Synthesis



Scheme 2. Synthesis of the Aromatic Condensation Polymer 3 in a Friedel−Crafts-Type Polyhydroxyalkylation of the Aromatic Monomer 2 with *N*-Methylisatin



Polymer Synthesis. A typical example of polymer preparation is as follows: Trifluoromethanesulfonic acid (0.65 mL) was added to a mixture of dichloromethane (3.9 mL), *N*-methylisatin (0.16 g, 1.04 mmol), and 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene (**2**) (0.55 g, 1.04 mmol). The reaction mixture was stirred for 2 h at room temperature and poured slowly into methanol. The white polymer fibers formed were filtered off and washed with hot methanol. After drying, 0.65 g (92.5%) of a white fibrous polymer (**3**) was obtained. The inherent viscosity of the 0.2% solution of the polymer in NMP at 25 °C was 0.89 dL g^{-1}.

Results and Discussion. Monomer **2** (1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene) was synthesized in a moderate yield (42%) starting from 9,9-dimethylfluorene-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**) and 1,4-dibromo-2,3,5,6-tetrafluorobenzene in a standard Suzuki-type aryl−aryl cross-coupling (Scheme 1). Analysis of the monomer has confirmed its structural integrity and high purity (see Experimental Section).

Applying standard Friedel−Crafts conditions (e.g., $AlCl_3$ in methylene chloride or CS_2)[13] led neither to a regioselective coupling nor to high molecular weight products. However, our recent reports on superacid-catalyzed Friedel−Crafts-type

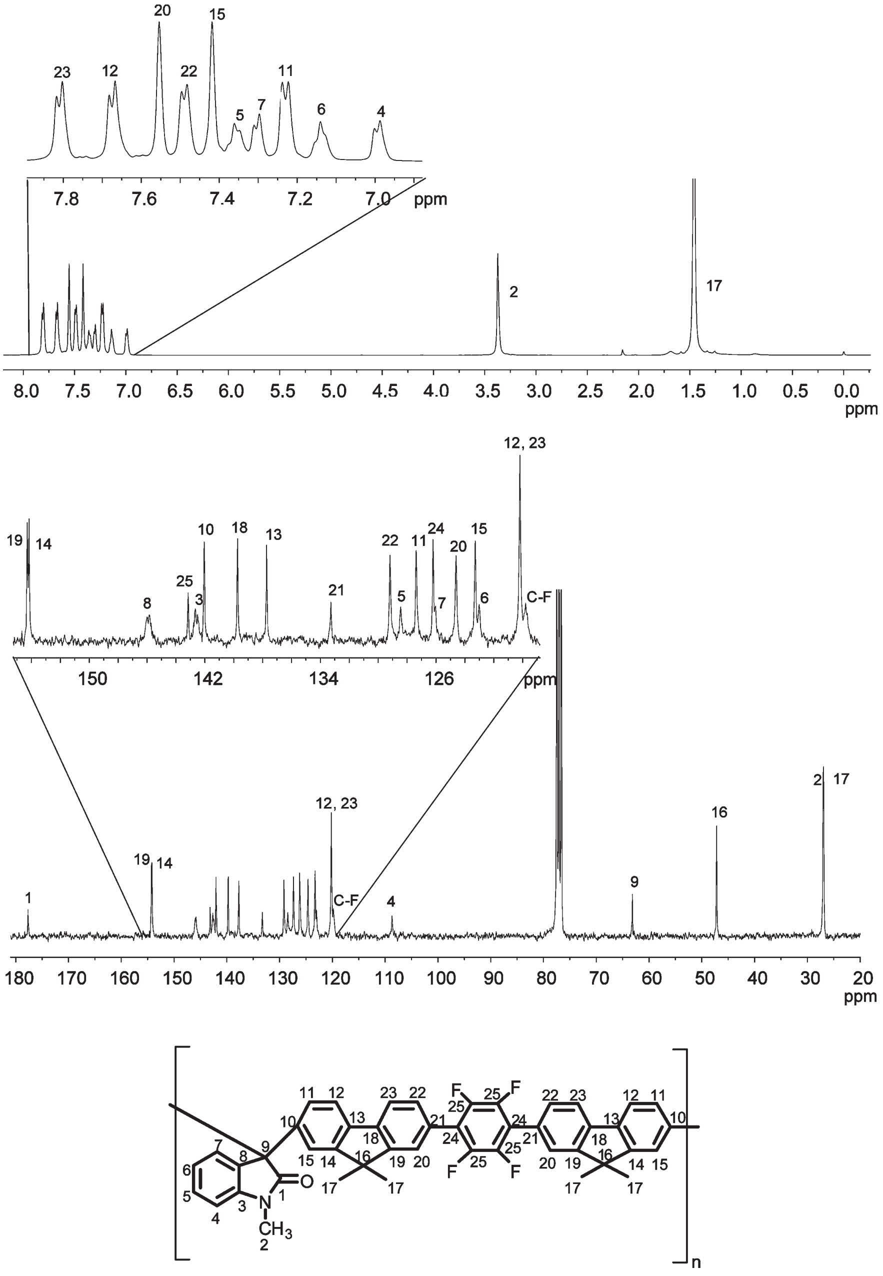


Figure 1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of polymer **3** (solutions in $CDCl_3$). The assignment of the signals is given in relation to the numbering in the depicted structure formula of **3**.

polycondensations impressively demonstrated the regioselective formation of linear, high molecular weight polymers.[14-16] Moreover, it is also important to note that this reaction scheme allows for the preparation of metal-free polymers of very high structural regularity.

Commercially available *N*-methylisatin was chosen as the hydroxymethylation component (carbonyl electrophile) for the coupling with the bifunctional aromatic monomer 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene (**2**). It should be noted that derivatives of isatin were already successfully used in the superacid-catalyzed syntheses of hyperbranched polymers.[17-19] First exploratory reactions of *N*-methylisatin with monomer **2** in pure trifluoromethylsulfonic acid (TFSA) or in a mixture of methylene chloride and TFSA obviously led to polymeric products (Scheme 2). Hereby, the syntheses in a mixture of methylene chloride as solvent and TFSA is preferred since it allows for a better control of the progress of the polycondensation and was, therefore, further used in our polymer preparations. The reactions were carried out at room temperature in 0.5–1 g batches. A white and fibrous, solid material of **3** was obtained after precipitating the liquid reaction mixture into methanol and washing/extraction of the raw product with hot methanol and acetone.

Polymer **3** as obtained in the superacid-catalyzed polycondensation is fully soluble in chlorinated and dipolar aprotic solvents as chloroform, tetrachloroethane, dimethylformamide, and dimethyl sulfoxide or strong acids as TFSA, but insoluble in aliphatic alcohols or acetone. Transparent and flexible films can be drop- or spin-cast from solutions of polymer **3**. The high solubility of polymer **3** may be caused by the kinked backbone and allowed us to perform reliable spectral studies to delineate its structure. Remarkably, polymer **3** possesses a very high molecular weight and a reasonably narrow polydispersity (polydispersity index, PDI): weight and mean average molecular weights M_w and M_n of polymer **3** were found to be 336 000 and 212 000 g/mol,

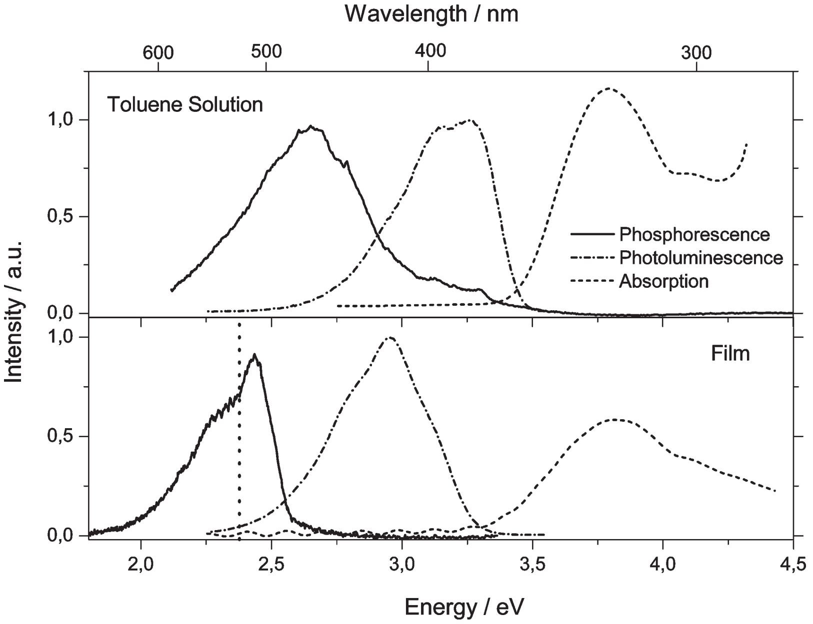


Figure 2. Optical spectra of **3** in toluene solution and in the solid state: absorption (dashed), fluorescence (dash-dotted), and phosphorescence (solid); the dotted line in the solid-state phosphorescence spectrum indicates the triplet energy level of the phosphorescent dopant Ir(mppy)$_3$ at 2.38 eV that is used in the following PhoLED experiments.

respectively (PDI: 1.58). In thermogravimetric measurements (TGA) the temperature of 2% weight loss in air was found to be ~400 °C. DSC analysis did not reveal any thermal transitions before decomposition of the polymer starts. The density of polymer **3** was found to be 1.157 g/cm^3.

The ^{1}H NMR and ^{13}C NMR spectra of the polymer **3** (Figure 1) are well resolved, and all signals related to the 7,7′-disubstituted 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene and *N*-methylindol-2-one fragments are evident. Detail analysis of these spectra revealed no essential indications of structural irregularities.

Polymer **3** shows a long wavelength absorption maximum $\lambda_{\max}$ at 328 nm in toluene solution (Figure 2), which is slightly blue-shifted to 325 nm in the solid state (thin film). The solid-state absorption band (optical bandgap energy ca. 3.35 eV) is somewhat broadened probably due to an increased conformational disorder. The energetic position of the long-wavelength absorption band is mainly determined by the longest π-conjugated pentaphenyl segment (1,4-bis-(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene) of the nonconjugated condensation polymer.

The corresponding photoluminescence (PL) maxima are found at ca. 380 nm (3.26 eV; toluene solution) and 418 nm (2.97 eV; solid state). The red shift of the solid state PL maximum indicates some interchain interactions (aggregate formation). The triplet emission bands have been recorded by time-gated PL spectroscopy and peak at 2.66 eV (466 nm; toluene solution) and 2.40 eV (517 nm; solid state). The HOMO level of polymer **3** (work function) was estimated to 5.97 eV by UV photoelectron spectroscopy (Riken AC-2). The herein reported energy levels suggest a certain potential of polymer **3** as matrix material for solution-processed green and red phosphorescent organic light emitting diodes (PhoLEDs).

Therefore, PhoLEDs were fabricated with polymer **3** as host for the well-known green emitting dopant Ir(mppy)$_3$. The general device structure was ITO/PEDOT (35 nm)/HTL 1 (40 nm)/HTL 2 (10 nm)/polymer **3** with 3−10% (w/w) Ir(mppy)$_3$ as dopant (60 nm)/CsF (2 nm)/Al (100 nm). HTL 1 and HTL 2 are graded triarylamine-based, cross-linkable hole transport layers; for chemical structures see ref 12. Figure 3 shows the current and EL brightness as well the luminous efficiency as a function of voltage for the fabricated PhoLEDs. An increase of the current density can be observed with rising emitter concentration. Therefore, it can be expected that the emitter plays a significant role in the charge transport, in particular for holes. However, at dopant concentrations higher than 7 wt %, the device efficiency is reduced from 17.5 to 13.6 cd/A due to the disproportional increase of current and luminous density.[20] The triplet energy of the green emitting dopant Ir(mppy)$_3$ (2.38 eV)[21] is only slightly lower than the relaxed triplet energy of **3** (see Figure 2, dashed line) which may cause a certain amount of triplet back transfer to the matrix;[22] however, it should be noted that the nonrelaxed triplet energy of the polymer will be typical 100−150 meV higher than this, and it is this energy which dictates energy transfer.[11] Nevertheless, the obtained maximum efficiency of ca. 17.5 Cd/A at 5 V for a dopant concentration of 7 wt % Ir(mppy)$_3$ (Figure 3) impressively illustrates the high potential of this class of (co)polymers as PhoLED matrix material. This value compares very well to that obtained using a much more complex copolymer containing carbazole and oxadiazole moieties reported by Diken et al.[23] which had very low molecular weight compared to our new polymer **3**. On the other hand, a similar device using a blend of a hole-transporting polymer and an electron-transporting low molecular weight compound—poly(*N*-vinylcarbazole) (PVK) and 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD)—as matrix material and 6 wt % Ir(mppy)$_3$ yielded an current efficiency of ca. 33 Cd/A at 5 V.[12] However, the PVK−PBD couple generally leads to devices with low operational lifetime.[24] Initial stability tests with the **3** as matrix polymer showed improved device stability in comparison to devices with poly(*N*-vinylcarbazole)-based matrices.

The electroluminescence (EL) spectra of the PhoLED devices (Figure 4) are fully independent from the dopant concentration in the investigated range of dye loading (3−10% w/w) and the applied voltage and always resemble the EL spectrum of the dopant Ir(mppy)$_3$ (EL maximum: ca. 519 nm) without any

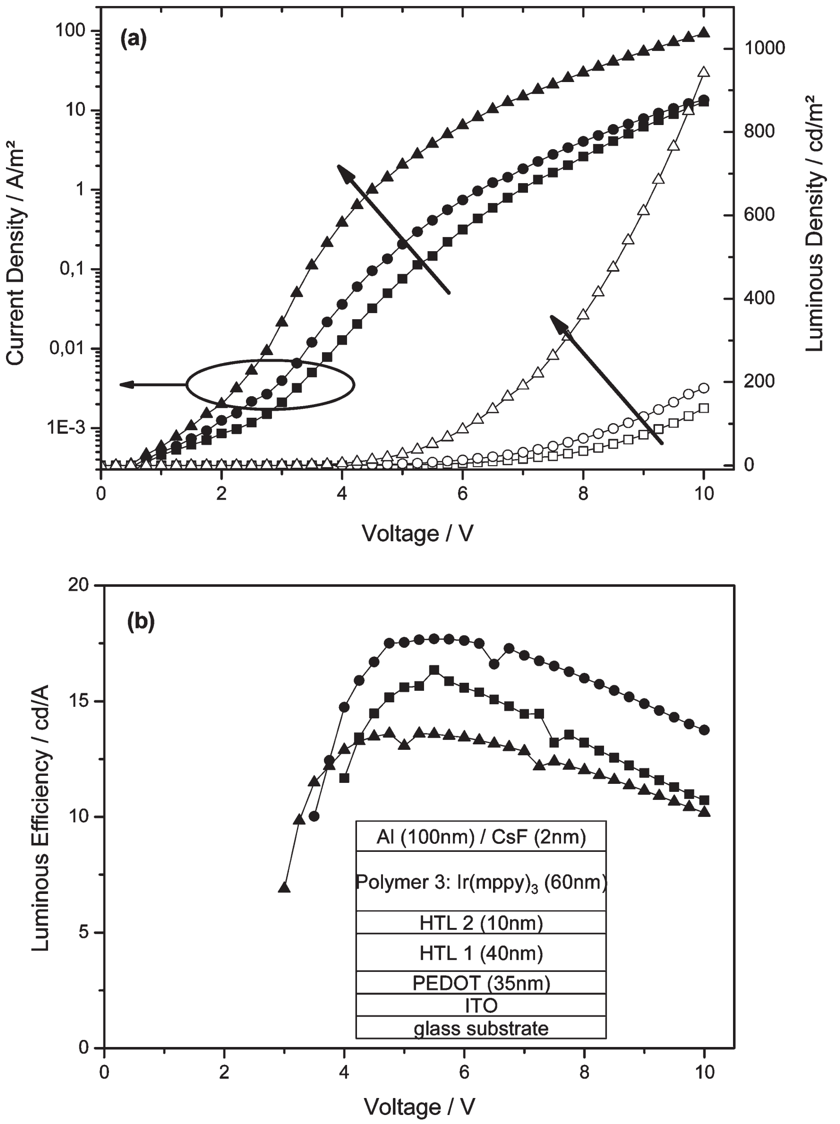


Figure 3. (a) Current (closed symbols) and luminous (open symbols) density and (b) luminous efficiency as a function of voltage for the three PhoLEDs with 3 (■), 7 (●), and 10 wt % (▲) Ir(mppy)$_3$ in polymer **3**. The device structure is shown as an inset.

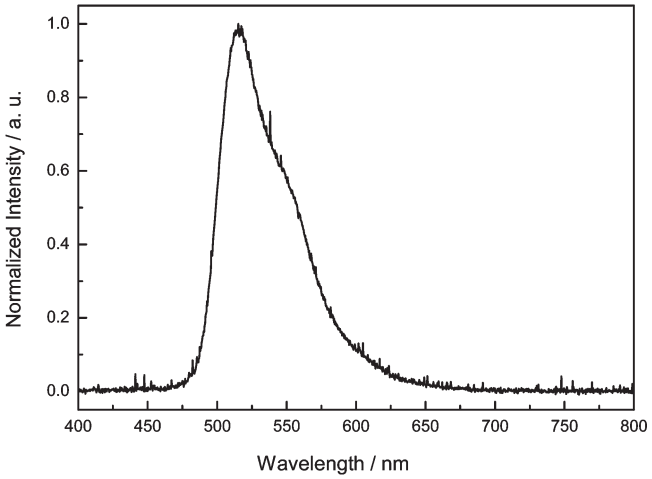


Figure 4. Normalized EL spectrum of the investigated PhoLED devices. The spectrum is representative for all measured devices within a range of 6−10 V and 3−10 wt % dye content in copolymer **3**.

high-energy emission components caused by singlet PL from the matrix at wavelengths <475 nm ($\lambda_{\max,\mathrm{PL}}$ of **3**: 418 nm).

Conclusion. The superacid-catalyzed Friedel−Crafts-type polycondensation of 1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene (**2**) as bifunctional, nonactivated aromatic monomer and *N*-methylisatin as bifunctional keto electrophile allows for the generation of high molecular weight aromatic polymers with conjugated blocks of defined length within the main chain. Polymer **3** with partially fluorinated pentaphenyl blocks as most extended conjugated segment (1,4-bis(9,9-dimethylfluoren-2-yl)-2,3,5,6-tetrafluorobenzene) exhibits electronic energy levels that allow a combination of **3** as matrix polymer with green and red emitting iridium-based organometallic phosphors in solution-processed phosphorescent, organic light emitting diodes (PhoLEDs). With Ir(mppy)$_3$ as green emitting phosphor a very promising maximum EL efficiency of 17.5 Cd/A has been observed. Hereby, the pure emission of the phosphor is detected without any high-energy emission components of the matrix. The electroluminescence (EL) spectra of the PhoLED devices have been independent from the dopant concentration (3−10% w/w) and the applied voltage. Using the newly developed polycondensation scheme, structurally related polymers are currently prepared and tested in PhoLED devices.

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