ADVANCED MATERIALS

Supporting Information

High Triplet Energy Poly(9,9'-bis(2-ethylhexyl)-3,6-fluorene) as Host for Blue and Green Phosphorescent Complex **

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Synthesis of the monomer: *3,6-dibromo-9,9'-bis(2-ethylhexyl)fluorene*

3,6-dibromophenanthrenequinone (**2**): Dry bromine (70.3 g, 440 mmol) was added dropwise over 1.5 h into magnetically stirred solution of compound **1** (41.6 g, 200 mmol) in dry nitrobenzene (250 mL) at 130 °C under the tungsten lamp. After complete addition, the reaction mixture was heated at 130 °C during 20 h. The product was washed extensively with anhydrous ethanol and used without further purification. Yield: 70.8g (96.7%) of yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.14 (d, *J*= 1.5 Hz, 2H), 8.09 (d, *J*= 8.3 Hz, 2H), 7.69 (dd, *J*= 1.5 Hz, *J*= 8.3 Hz, 2H). Anal. Cacld for $C_{14}H_6Br_2O_2$: C 45.94, H 1.65, N 14.47; found: C 46.05, H 1.71, N 14.54.

3,6-dibromofluorenone (**3**): Compound **2** (13.0 g, 35.5 mmol) was gradually added to a solution of KOH (56 g, 1 mol) in water (250 mL) at 85 °C. The reaction mixture was stirred for a further period of 5 h at the same temperature. Powdered $KMnO_4$ (29 g, 185 mmol) was gradually added over 1 h. After complete addition, the mixture was boiled for 2 h, cooled, washed and filtered. The residue was suspended in water and boiled with enough $NaHSO_3$. The left solid was collected and dried. Soxhlet extractions were performed with toluene to give yellow glistening flakes. The product was used without further purification. Yield: 9.7 g (80.8%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.71 (d, *J*= 1.5 Hz, 2H), 7.58 (d, *J*= 8.0 Hz, 2H), 7.52 (dd, *J*= 1.5 Hz, 8.0 Hz, 2H). Anal. Calcd for $C_{13}H_6Br_2O$: C 46.20, H, 1.79; found: C 46.04, H 1.84.

3,6-dibromofluorene (**4**): Zn powder (32 g, 0.5 mol) was added immediately to a solution of $HgCl_2$ (3.4 g, 12.5 mmol) and concentrated HCl (3 mL) in water (80 mL) , stirred

vigorously for 15min. The liquid phase was decanted and washed with distilled water. Compound **3** (10 g, 29.6 mmol), toluene (40 ml) and concentrated HCl (36 ml) were mixed and refluxed for 26 h. Meanwhile extra concentrated HCl (10 ml) was added every six hours. The organic phase was separated and the aqueous phase was extracted with dichloromethane (2×30 mL). The combined organic phases were washed with saturated aqueous sodium bicarbonate, dried with brine and magnesium sulfate and evaporated. The crude product was purified by column chromatography (hexane: ethyl acetate = 15: 1) on silica gel to give a white solid. Yield: 2.5g (26.1%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.84 (d, *J*= 1.8 Hz, 2H), 7.43 (dd, *J*= 1.8, 8.0 Hz, 2H), 7.38 (d, *J*= 8.0 Hz, 2H), 3.77 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 142.59, 142.18, 130.20, 126.49, 123.35, 120.99, 36.25. EI-MS: cacld. for [M^+] $C_{13}H_8{}^{79}Br_2$, m/z 322; found, m/z 322. Anal. calcd for $C_{13}H_8Br_2$: C 48.19, H 2.49; found: C 48.70, H 2.59.

3,6-dibromo-9,9'-bis(2-ethylhexyl)fluorene (**5**): Sodium hydride (60% dispersion in mineral oil; 2.1 g, 52.5 mmol) was washed THF (2×30 mL). Compound **4** (4 g, 12.3 mmol) was added to a stirred suspension of the sodium hydride in THF (30 mL). The resultant mixture was stirred for 0.5 h at room temperature under argon atmosphere. 1-bromo-2-ethylhexane (5.4 g, 28 mmol) was added dropwise to the mixture over 1 h. After complete addition, the mixture was heated to boil for 24 h. The mixture was adjusted to pH= 7 with diluted hydrochloric acid and extracted with dichloromethane (2×30 mL). The combined organic phases were washed with saturated aqueous sodium chloride, dried with magnesium sulfate and evaporated. The residual 1-bromo-2-ethylhexane was distilled off under reduced pressure. The crude product was purified by column chromatography (hexane) to give a colourless oil. Yield: 6.50 g (96.0%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.80 (d, *J*= 1.8 Hz, 2H), 7.24-7.45 (m, 4H), 1.99-1.87 (m, 4H), 0.39-0.97 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 149.49, 142.04, 129.93, 125.56, 123.12, 120.82, 54.79, 44.32, 34.56, 33.72, 28.10, 26.86, 22.66, 13.92, 10.16. APCI-MS: cacld. for [M^++H] $C_{29}H_{40}{}^{79}Br_2$, m/z 547; found, m/z 547.

Characterization: Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1_M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. All measurements were calibrated against ferrocene which has an ionization potential of 4.8 eV under vacuum. Thermogravimetric analysis (TGA) was carried out under nitrogen purging at a heating rate of 20 °C/min from 30 to 800 °C. DSC analyses were performed at a heating rate of 20 °C/min from -30 to 300 °C under nitrogen purging. The triplet energies were obtained as the maximum of the first vibronic transtion ($S_0^{v=0} \leftarrow T_1^{v=0}$) of the phosphorescence spectra.[S1] The thin film sample was spun cast from the solution of the polymer **6** and attached to a cryostat (T= 11 K). The sample was excited by a ps pulsed He-Cd laser at 325 nm. The photoluminescence measurement system consist of the monochromator (Acton SpectraPro 500i) attached with a photomultiplier tube (PMT) (Hamamatsu R636-10) as the detector. The signal from PMT is first pre-amplified by the pre-amplifier (Princeton Applied Research 5182), then it is processed by the lock-in amplifier (Stanford Research Systems SR830 DSP Lock-in Amplifier) and recorded by the computer.

Fabrication and characterization of PLEDs: Patterned indium tin oxide (ITO) coated glass substrates were cleaned with acetone, detergent, distilled water, and 2-propanol subsequently, in an ultrasonic bath. After treatment with oxygen plasma, 50 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P4083, Bayer AG) was spin-coated onto the substrate followed by drying in a vacuum oven at 80 °C for 8 h. Poly(vinylcarbazole) (PVK, Aldrich) from 1, 1, 2, 2-tetrachloroethane solution was spin-coated onto PEDOT. A toluene solution of P36EHF or a chlorobenzene solution of 10 wt-% FIrpic in **6** was prepared, filtered through a 0.45 μm filter, and spin-coated over the

PVK or PEDOT layer in a dry box. The film thickness of the active layers was around 80 nm, as measured with an Alfa step 500 surface profiler (Tencor). The electron-injection/hole-blocking layer, 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI) was then vapor deposited in a vacuum of below $1x10^{-4}$ Pa (only for the undoped neat P36EHF). Ba and Al layers were vacuum-evaporated on the top of an EL polymer layer or TPBI layer under a vacuum of $1x10^{-4}$ Pa. Device performances were measured in a dry box. Current-voltage (*I*-*V*) characteristics were recorded with a Keithley 236 source meter. EL spectra were recorded with a photodiode calibrated by using a PR-705 SpectraScan Spectrophotometer (Photo Research). External quantum efficiency was verified by measurement in the integrating sphere (IS080, Labsphere) after encapsulation of the devices with UV-cured epoxy and thin cover glass.

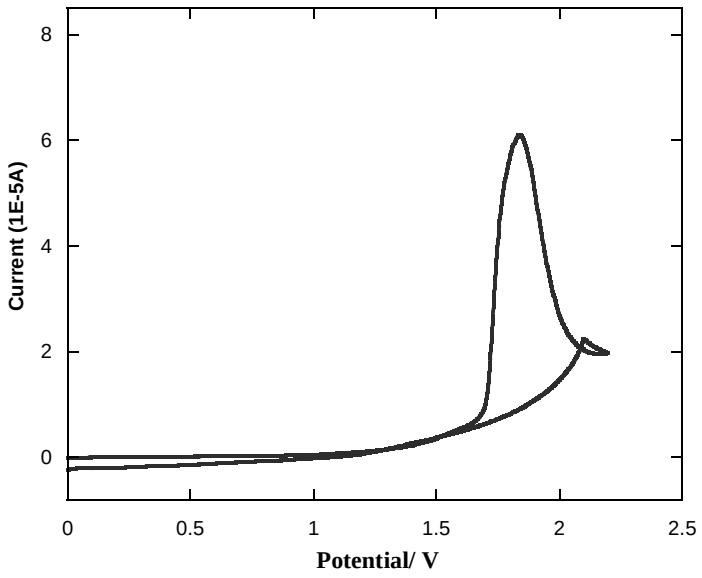

Figure S1. Cyclic voltammogram of P36EHF in 0.1M Bu_4NPF_6/ CH_3CN solution

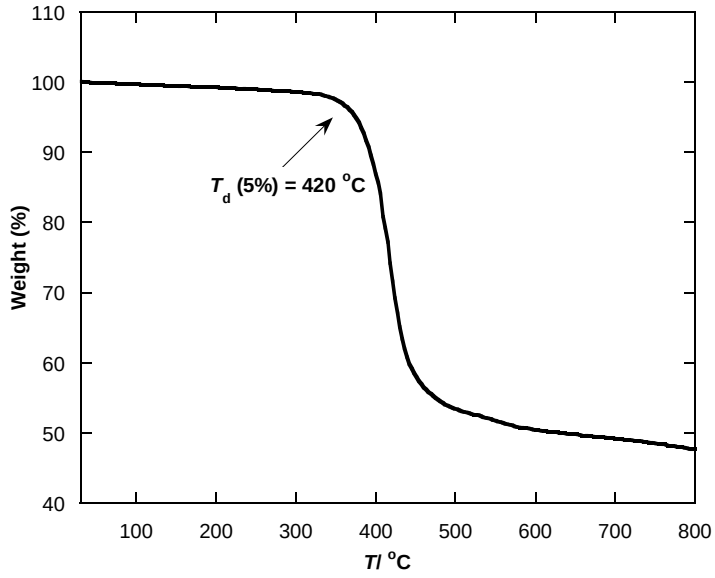

Figure S2. Thermogravimetric analysis (TGA) for P36EHF

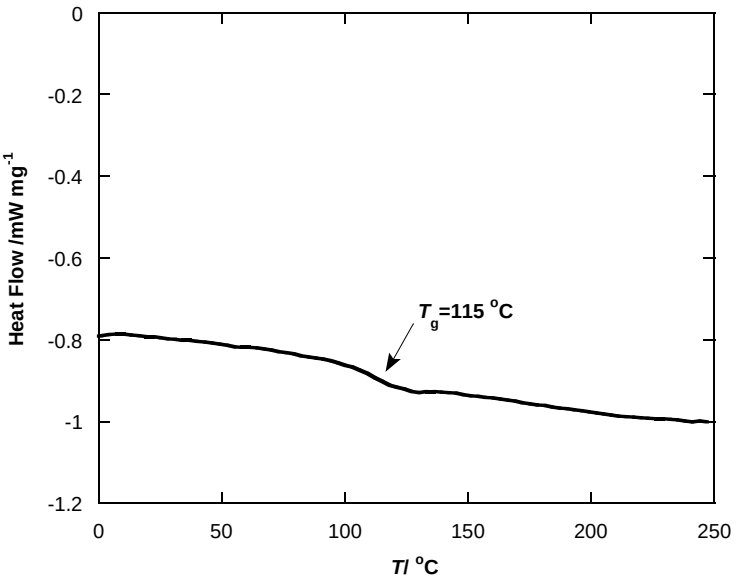

Figure S3. Differential scanning calorimetry (DSC) for P36EHF

References

[S1] A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel and K. Brunner, *J. Am. Chem. Soc.* **2004**, *126*, 7718.