Electronic Supplementary Information (ESI)

A tetraphenylethene-based red luminophor for efficient non-doped electroluminescence device and cellular imaging

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General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compound **1**[1] and **3**[1] were prepared according to the literature methods. All other chemicals and reagents were purchased from Aldrich and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated chloroform using tetramethylsilane (TMS; δ = 0) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer. High resolution mass spectra were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDT-TOF mode. Thermogravimetric analysis was carried on a TA TGA Q5000 under dry nitrogen at a heating rate of 10 ^{o}C/min. Thermal transitions were investigated by differential scanning calorimetry

using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min. The ground-state geometries were optimized using the density functional (DFT) with B3LYP hybrid functional at the basis set level of 6-31G (d). All the calculations were performed using Gaussian 03 package. Cyclic voltammetry was performed on a CHI660A electrochemical work station at room temperature with use of a standard three-electrode electrochemical cell in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. The working and reference electrodes were platinum and Ag/AgCl. The reference electrode was checked versus ferrocene as internal standard as recommended by IUPAC. All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements.

Device fabrication

The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of 25Ω/□. Prior to load into the pretreatment chamber, the ITO-coated glasses were soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned samples were treated by perfluoromethane (CF_4) plasma with a power of 100 W, gas flow of 50 sccm, and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr for the deposition of *N*,*N*-bis(1-naphthyl)-*N*,*N*-diphenylbenzidine (NPB), emitter, 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi), which served as hole-transporting, light-emitting, hole-blocking, and electron-transporting layers, respectively. The samples were then transferred to the metal chamber for cathode deposition which composed of lithium fluoride (LiF) capped with aluminum (Al). The light-emitting area was 4 mm^2. The current density-voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiency of the device were inferred from the photocurrent of the photodiode. The electroluminescence spectra were obtained by a PR650 spectrophotometer. All measurements were carried out under air at room temperature without device encapsulation.

Synthesis of TTPEBTTD-DSPE NPs

The TTPEBTTD-DSPE NPs were prepared through a modified nanoprecipitation method according to our previous published paper.[2] Briefly, 1 mL of THF solution containing 1 mg of TTPEBTTD and 2 mg of mixture of DSPE-PEG_{2000} was poured into 9 mL of water. This was followed by sonicating the mixture for 60 seconds at 12 W output using a microtip probe sonicator (XL2000, Misonix Incorporated, NY). The emulsion was then stirred at room temperature overnight to evaporate THF. The obtained solution was filtered using a 0.20 μm syringe-driven filter to collect the products.

Cell culture and imaging

MCF-7 breast cancer cells were cultured in folate-free Dulbecco's Modified Eagle Medium (DMEM) containing 10% fetal bovine serum and 1% penicillin streptomycin at 37 °C in a humidified environment containing 5% CO_2. Before experiment, the cells were pre-cultured until confluence was reached. MCF-7 breast cancer cells were cultured in the confocal imaging chambers (LAB-TEK, Chambered Coverglass System) at 37 °C. After 80% confluence, the medium was removed and the adherent cells were washed twice with 1 × PBS buffer. The TTPEBTTD-DSPE NPs in FBS-free DMEM medium at 2 μM of TTPEBTTD were then added to the chambers. After incubation for 2 h, the cells were washed three times with 1 × PBS buffer and then fixed by 75% ethanol for 20 minutes, which were further washed twice with 1 × PBS buffer and stained by DAPI for 10 min. The cell monolayer was then washed twice with 1 × PBS buffer and imaged by confocal laser scanning microscope (CLSM, Zeiss LSM 410, Jena, Germany) with imaging software (Olympus Fluoview FV1000) under the same experimental condition. The fluorescent signal was collected upon 488 nm excitation with a 560 nm longpass barrier filter.

Cytotoxicity of TTPEBTTD-DSPE NPs

MTT assays were performed to assess the metabolic activity of MCF-7 breast cells. MCF-7 cells were seeded in 96-well plates (Costar, IL, USA) at an intensity of 4×10^4 cells mL^{-1}. After 24 h incubation, the medium was replaced by the TTPEBTTD-DSPE NPs suspension at TTPEBTTD concentrations of 1, 5, and 10 μM, and the cells were then incubated for 24, 48, and 72 h, respectively. To eliminate the UV absorbance interference of TTPEBTTD-DSPE NPs at 570 nm, the cells were also incubated with the same series of doses of TTPEBTTD-DSPE NPs as the control. After the designated time intervals, the

wells were washed twice with 1 × PBS buffer, and 100 μL of freshly prepared MTT (0.5 mg mL^{-1}) solution in culture medium was added to each well. The MTT medium solution was carefully removed after 3 h incubation in the incubator. Isopropanol (100 μL) was then added into each well, and the plate was gently shaken for 10 min at room temperature to dissolve all precipitates formed. The absorbance of MTT at 570 nm was monitored by the microplate reader (Genios Tecan). Cell viability was expressed by the ratio of absolute absorbance of the cells incubated with NP suspension to that of the cells incubated with culture medium only.

Synthesis

4-(5-Bromothiophen-2-yl)-7-(3,5-dibromothiophen-2-yl)benzo-2,1,3-thiadiazole (2): A mixture of **1** (0.3 g, 1 mmol), NBS (1.07 g, 3 mmol) and BPO (0.03 g, 0.15 mmol) in CCl_4 (100 mL) was heated to reflux for 36 h. After cooling to room temperature, the precipitate was separated from the mixture. After washing with hot chloroform for several times, orange solid of **2** was obtained in 25% yield (0.13 g). m.p. 175–177 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.05 (d, 1H, J = 7.5 Hz), 7.88–7.85 (m, 2H), 7.17 (d, 1H, J = 3.9 Hz), 7.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 154.1, 152.6, 141.0, 134.1, 131.6, 130.7, 128.6, 127.6, 125.2, 124.2, 116.1, 115.4, 110.0. HRMS: m/z 535.7145 (M^+, calcd 535.7165).

4-{3,5-Bis[4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl]-7-{5-[4-(1,2,2-triphenylvinyl)phenyl] thiophen-2-yl}benzo-2,1,3-thiadiazole (TTPEBTTD): A mixture of **2** (0.54 g, 1 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**3**) (1.5 g, 4 mmol), $Pd(PPh_3)_4$ (0.16 g, 0.15 mmol), and potassium carbonate (1.6 g, 12 mmol) in 150 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 24 h under nitrogen. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. Red solid of TTPEBTTD was obtained in 56% yield (0.72 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.11 (d, 1H, J = 3.6 Hz), 7.70–7.66 (m, 2H), 7.48–7.34 (m, 6H), 7.13–6.89 (m, 53H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 154.6, 152.9, 146.2, 145.5, 144.4, 144.3, 144.2, 144.1, 143.4, 142.6, 142.1, 141.8, 141.2, 141.0, 139.0, 135.5, 132.7, 132.6,

132.5, 132.0, 130.8, 129.5, 128.4, 127.3, 127.2, 126.8, 126.5, 125.6, 124.7. HRMS: *m*/*z* 1290.4039 (M^+, calcd 1290.4075).

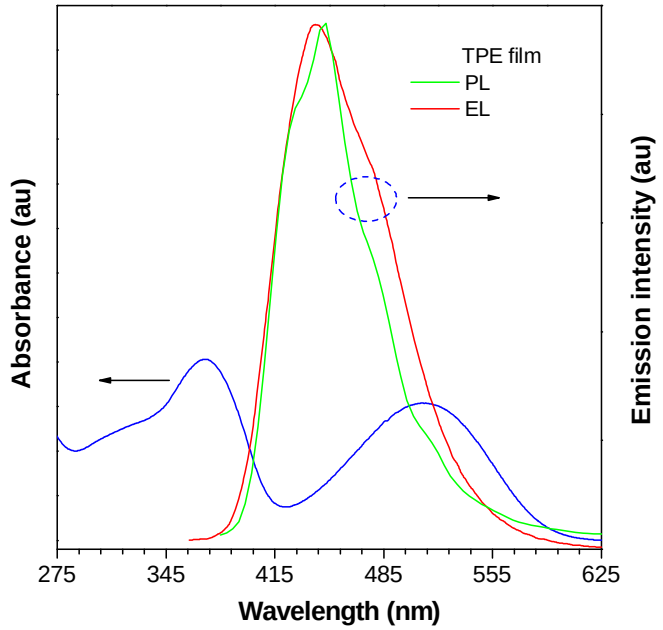

Fig. S1 Absorption spectrum of BTPEBTTD in THF solution and PL and EL spectra of TPE film.

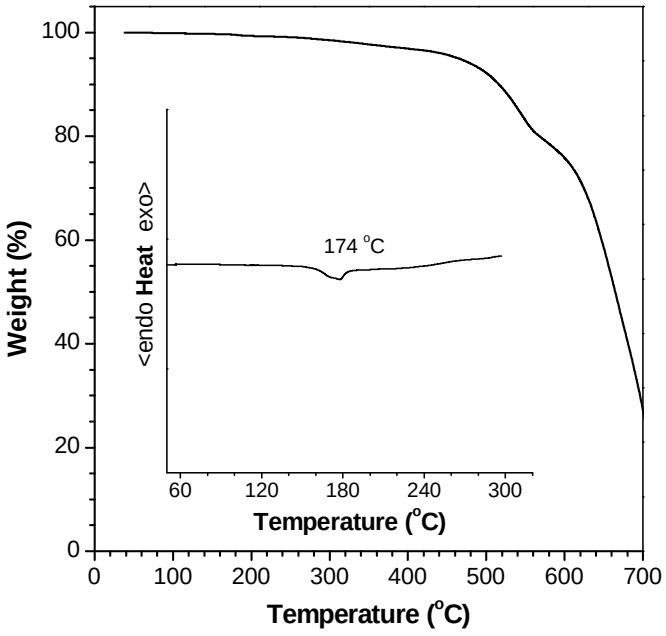

Fig. S2 TGA thermogram of TTPEBTTD recorded under nitrogen at a heating rate of 10 °C/min. Insert: DSC curve recorded during the second heating scan.

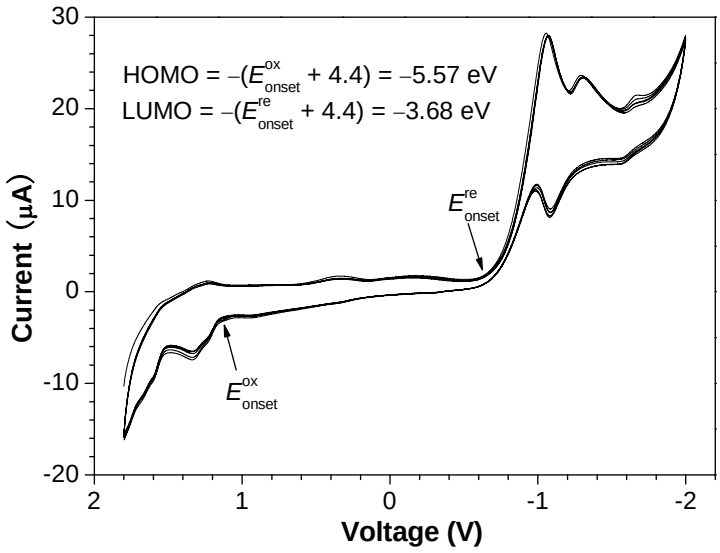

Fig. S3 Cyclic voltammogram of TTPEBTTD measured in dichloromethane containing 0.1 M Bu_4NPF_6, scant rate 100 mV/s.

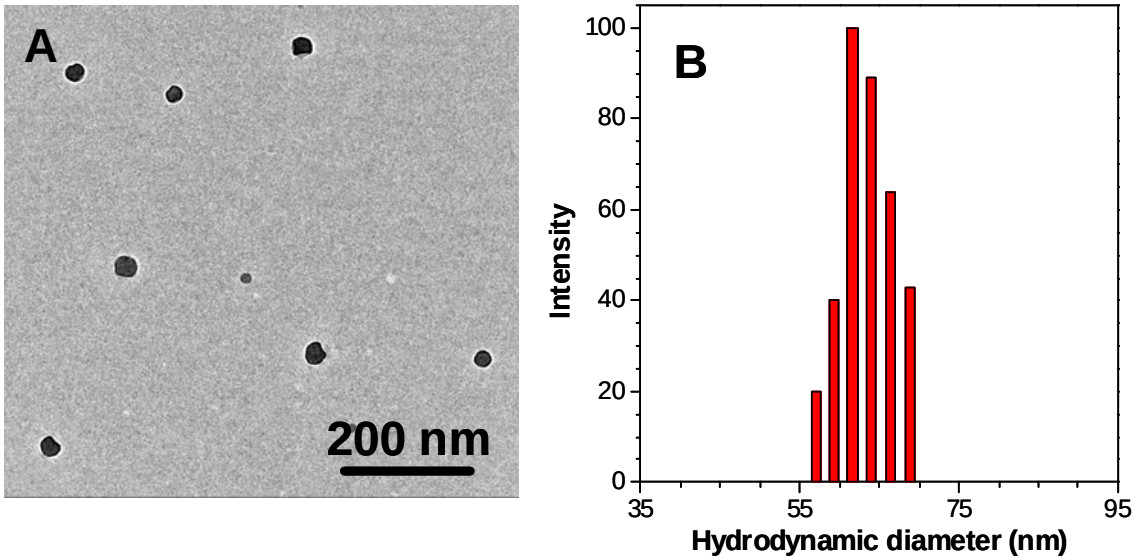

Fig. S4 (A) High resolution TEM image of TTPEBTTD-loaded DSPE NPs. (B) Particle size distribution of TTPEBTTD-DSPE NPs in water.

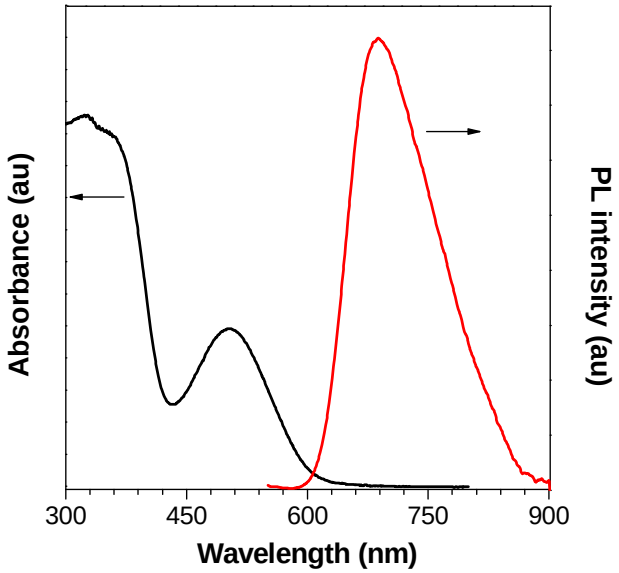

Fig. S5 Absorption and PL spectra of TTPEBTTD-DSPE NPs.

References

1. Z. Zhao, C. Deng, S. Chen, J. W. Y. Lam, W. Qin, P. Lu, Z. Wang, H. S. Kwok, Y. Ma, H. Qiu and B. Z. Tang, *Chem. Commun.*, 2011, **47**, 8847.
2. K. Li, Y. Jiang, D. Ding, X. Zhang, Y. Liu, J. Hua, S.-S. Feng and B. Liu, *Chem. Commun.*, 2011, **47**, 7323.