

Electronic Supplementary Information (ESI)

Aggregation-Induced Emission, Self-Assembly, and Electroluminescence of 4,4'-Bis(1,2,2-triphenylvinyl)biphenyl

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Experimental Section

Materials and instrumentations. THF was distilled from sodium benzophenone ketyl under nitrogen prior to use. All other chemicals and reagents were purchased

from Aldrich and used as received unless specified otherwise. Di(phenylethynyl)-diphenylsilane (**1**) and 1-(4-bromophenyl)-1,2,2-triphenylethylene (**3**) was prepared according to the published procedures.^{1,2}

¹H and ¹³C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated dichloromethane using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence spectra were recorded on a Perkin–Elmer LS 55 spectrofluorometer. MALDI–TOF mass spectrum was recorded on a GCT premier CAB048 mass spectrometer. High resolution electron micrographs were taken on a JEDL-100CX microscope. Samples were prepared by drop-casting dilute dispersion onto copper 400-mesh carrier grid covered with carbon-coated formvar film. The solvent was evaporated in open air at room temperature. Fluorescence micrographs were taken on an inverted fluorescence microscope (Nikon Eclipse TE2000-U); $\lambda_{\text{ex}} = 330\text{--}380$ nm, diachronic mirror = 400 nm. The images were captured using a digital CCD camera.

X-ray diffraction intensity data were collected at 100 K on a Bruker–Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo K α radiation. Multilayer electroluminescence (EL) devices were fabricated in the usual manner with sequential vacuum evaporation of various layers on 30 Ω/\square indium-tin oxide (ITO)-coated glass substrates. The ITO glasses were pre-cleaned in ultrasonic assisted detergent followed by rinsing with deionized water before being dried in oven at 100 °C. After 25 min of UV-ozone treatment, the substrates were transferred into a vacuum chamber with a base pressure of 2×10^{-4} pa for device fabrication. The EL spectra and the current–voltage–luminance characteristics of the EL devices were measured with a Spectrascan PR650 photometer and a computer-controlled HP4145B Semiconductor Parameter Analyzer under ambient conditions.

Synthesis of 4,4'-bis(1,2,2-triphenylethenyl)biphenyl (BTPE). The luminogenic compound was prepared according to the synthetic route shown in Scheme 1. A solution of lithium 1-naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (2.56 g, 20 mmol) and lithium granular (0.14 g, 20 mmol) in dry THF (30 mL) for 12 h at room temperature under nitrogen. A solution of **1** (1.9 g, 5 mmol) in

THF (20 mL) was then added dropwise into the solution of LiNaph, and the resultant mixture was stirred for 30 min at room temperature. The solution was cooled to -10°C , into which $\text{ZnCl}_2\text{-TMEDA}$ (6.3 g, 25 mmol) and 20 mL of THF were added. After the fine suspension was stirred for 1 h, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (100 mg) and a solution of **3** (4.1 g, 10 mmol) in 10 mL THF were added. After reflux for 12 h, the reaction was cooled to room temperature and terminated by addition of 2 M hydrochloric acid. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed successively with aqueous sodium chloride solution and water and then dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silicon-gel column chromatography using hexane as eluent. Recrystallization gave a white solid of BTPE in $\sim 60\%$ yield, based on the amount of **3** used.

M.p.: 290°C . ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.31 (d, 4 H, $J = 8.4$ Hz), 7.00–7.11 (m, 34 H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 144.44, 144.41, 144.39, 143.40, 141.70, 141.19, 138.90, 132.42, 132.07, 132.02, 128.43, 128.34, 128.30, 127.14, 127.08, 126.57. MS (MALDI-TOF): m/z 662.2151 (M^+ , 662.2974).

Preparation of Nanoaggregates. A stock solution of BTPE in THF (0.1 mM) was prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After adding appropriate amounts of THF, water was added dropwise under vigorous stirring to furnish 10 μM solutions with different fractions of water (f_w 0–99.5 vol %). Fluorescence spectra measurements of the resultant solutions were performed immediately.

References

- 1 S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem. Eur. J.*, 2000, **6**, 1683.
- 2 M. Banerjee, S. J. Emond, S. V. Lindeman and R. Rathore, *J. Org. Chem.*, 2007, **72**, 8054.

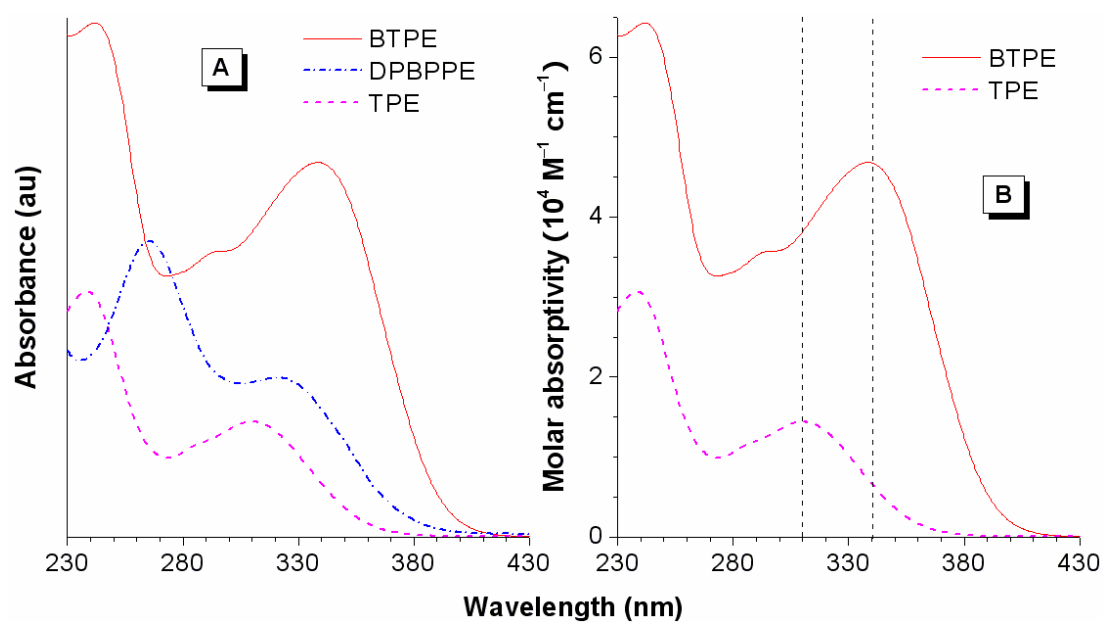


Fig. S1 UV spectrum of BTPE and TPE in THF and DPBPPE in acetonitrile (10 μ M).

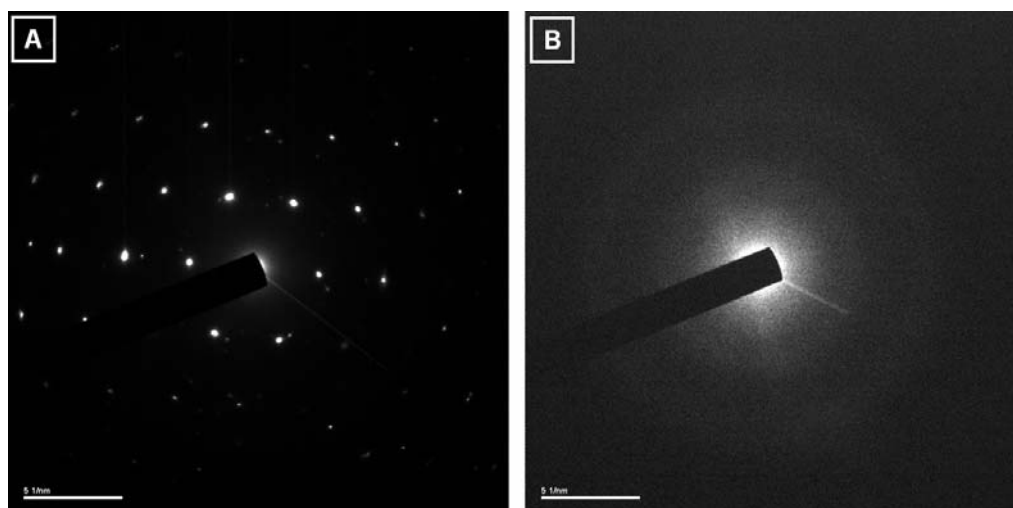


Fig. S2 ED patterns of (A) crystalline and (B) amorphous aggregates of BTPE formed in THF/water mixtures containing (A) 70% and (B) 80% water.

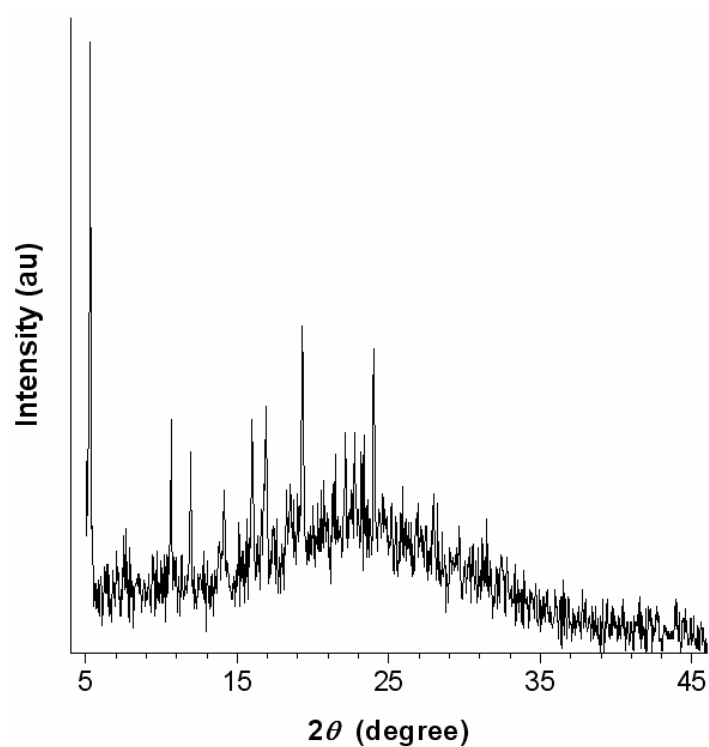


Fig. S3 XRD patterns of crystalline fibers of BTPE.

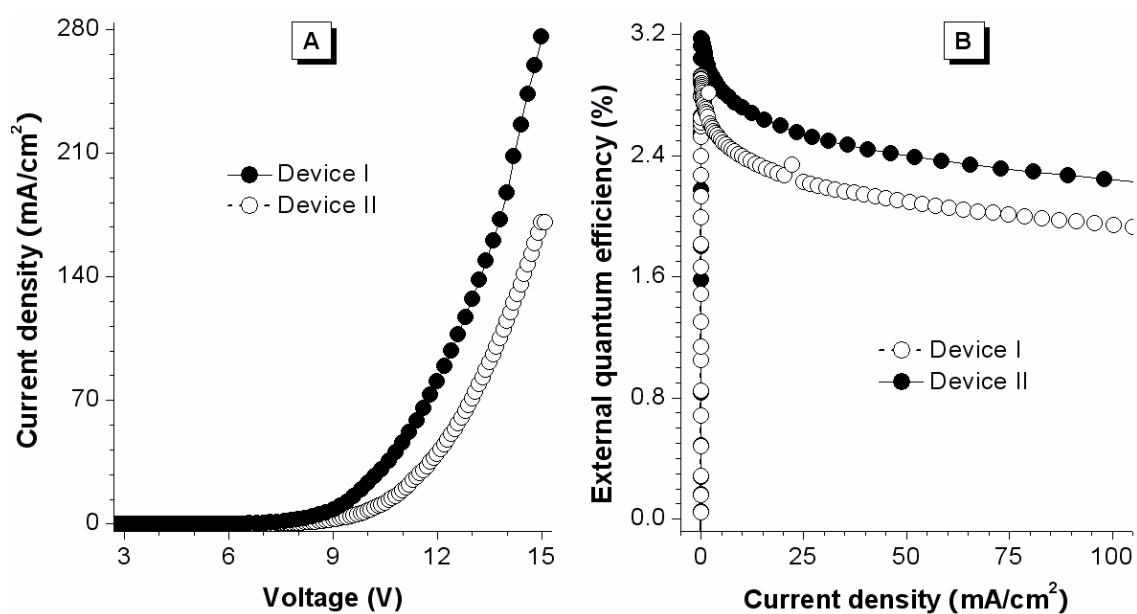


Fig. S4 Plots of (A) current density versus voltage and (B) external quantum efficiency versus current density for BTPE-based multilayer electroluminescence devices with a configuration of ITO/NPB/BTPE/TPBi/Alq₃/LiF/Al.