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Aggregation-enhanced emission and efficient electroluminescence of tetraphenylethene-cored luminogens

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General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. 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 400 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) 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.

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.

Preparation of nanoaggregates

Stock THF solutions of the luminogens with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water contents (0–99 vol %). The PL measurements of the resultant solutions were then performed immediately.

Synthesis

1,1,2,2-Tetrakis(4-bromophenyl)ethane (TPED-4Br): To a solution of 4,4'-dibromobenzophenone (**1**) (1.7 g, 5 mmol), zinc dust (0.78 g, 12 mmol) in 50 mL dry THF was added dropwise titanium(IV) chloride (1.15 g, 6 mmol) under nitrogen at –78 °C. After stirring for 20 min, the reaction mixture was warmed to room temperature and then heated to reflux for 12 h. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid TPE-4Br was obtained in 80% yield (1.3 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.26 (d, 8H, J = 8.4 Hz), 6.84 (d, 8H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 141.5, 139.6, 132.7, 131.3, 121.3. MS (EI): *m/z* 648 (M^+, calcd 648).

1,1,2,2-Tetrakis(4'-(1,2,2-triphenylvinyl)biphenyl-4-yl)ethene (PTPE): A mixture of TPE-4Br (0.65 g, 1 mmol), 4-(1,2,2-triphenylvinyl)phenylboronic acid (**2**) (2.3 g, 6 mmol), $Pd(PPh_3)_4$ (0.44 g, 0.4 mmol), and potassium carbonate (2.8 g, 20 mmol) in 200 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. Yellow solid of PTPE was obtained in 43% yield (0.71 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.37–7.32 (m, 16H), 7.12–7.02 (m, 76H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 144.4, 132.1, 132.0, 128.5, 128.4, 128.3, 127.2, 127.1. HRMS (MALDI-TOF): *m/z* 1653.7250 (M^+, calcd 1653.7233). Anal. Calcd for $C_{130}H_{92}$: C, 94.39; H, 5.61. Found: C, 94.31; H, 5.54.

1,2-Bis{4-(9,9'-spirobi[fluorene]-2-yl)phenyl}-1,2-bis{4-(9,9'-spirobi[fluorene]-7-yl)phenyl}ethene (TPE-4SF): The procedure was analogous to that described for PTPE. Yellow solid of TPE-4SF was obtained in 34 % yield (2.4 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.82–7.79 (m, 16H), 7.48 (d, 4H, J = 8.0 Hz), 7.36–7.32 (m, 12H), 7.09–7.04 (m, 20H), 6.83–6.81 (m, 12H), 6.71–6.67 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 149.3, 149.2, 148.7, 142.7, 141.8, 141.4, 140.9, 140.3, 139.9, 138.5, 131.6, 127.8, 127.7, 126.7, 126.1, 124.1, 124.0, 122.2, 120.2, 120.0, 66.0. HRMS (MALDI-TOF):

m/*z* 1589.5955 (M^+, calcd 1589.5981). Anal. Calcd for $C_{126}H_{76}$: C, 95.18; H, 4.82. Found: C, 95.11; H, 4.63.

4',4'',4''',4''''-(Ethene-1,1,2,2-tetrayl)tetrakis(*N*,*N*-diphenylbiphenyl-4-amine) (TPE-4TPA): The procedure was analogous to that described for PTPE. Yellow solid of TPE-4TPA was obtained in 36% yield (2.4 g). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.38 (d, 8H, *J* = 8.4 Hz), 7.28 (d, 8H, *J* = 8.4 Hz), 7.19–7.15 (m, 18H), 7.08–7.01 (m, 30H), 6.96–6.92 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 148.4, 147.8, 143.2, 139.0, 135.3, 132.6, 129.9, 128.2, 126.4, 125.0, 124.7, 123.5. HRMS (MALDI-TOF): *m*/*z* 1304.5764 (M^+, calcd 1304.5757). Anal. Calcd for $C_{98}H_{72}N_4$: C, 90.15; H, 5.56; N, 4.29. Found: C, 90.02; H, 5.51; N, 4.10.

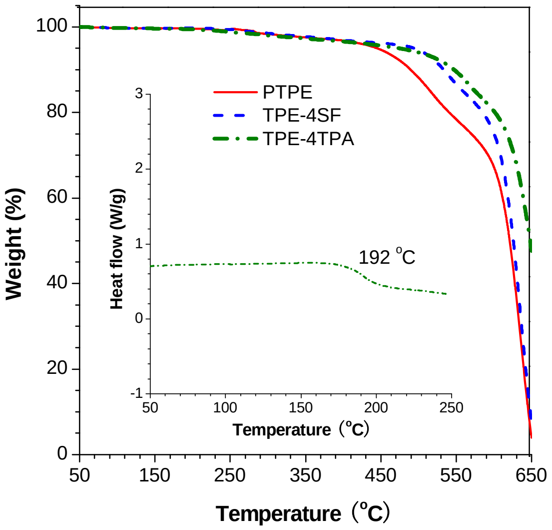

Fig. S1 TGA thermograms of TPE-cored luminogens recorded under nitrogen at a heating rate of 10 °C/min. Inset: DSC curve of TPE-4TPA (second heating).

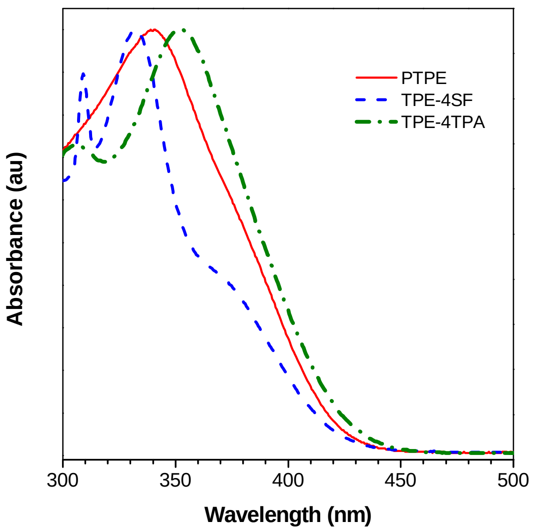

Fig. S2 Absorption spectra of TPE-cored luminogens in 1,4-dioxane solution.

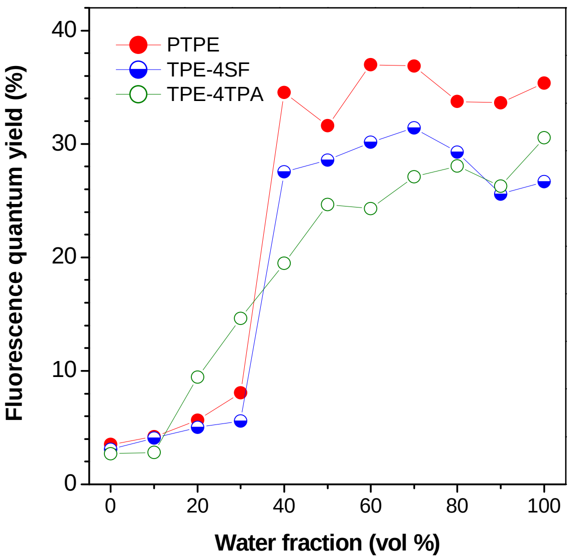

Fig. S3 Plots of fluorescence quantum yield *vs*. water fraction of TPE-cored luminogens in 1,4-dioxane/water mixtures with different water fractions.