

Electronic Supporting Information

Synthesis, Solvatochromism, Aggregation-Induced Emission and Cell Imaging of Tetraphenylethene-Containing BODIPY Derivatives with Large Stokes Shift

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Experimental Section

Materials

Tetrahydrofuran (THF), dichloromethane and toluene were distilled under normal pressure from sodium benzophenone ketyl or calcium hydride under nitrogen immediately prior to use. Dichlorobis(triphenylphosphine)palladium(II) [$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$], copper(I) iodide (CuI), tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$], potassium carbonate (K_2CO_3), palladium(II) acetate [$\text{Pd}(\text{OAc})_2$], tripotassium phosphate (K_3PO_4), tri-*tert*-butylphosphine (*t*- Bu_3P), *n*-hexane, 1,4-dioxane, chloroform, ethyl acetate (EA), dimethylformide (DMF), acetone, acetonitrile, ethanol, methanol and other chemicals and solvents were all purchased from Aldrich and used as received without further purification. Fetal bovine serum, penicillin and streptomycin were purchased from Invitrogen.

Instruments

IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ^1H , ^{11}B , ^{13}C and ^{19}F NMR spectra were measured on a Bruker ARX 300 or 400 NMR

spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. UV-vis absorption spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The ground state geometries of TPB, TPVB and TPEB were optimized by density functional theory (DFT). The DFT calculations were carried out using B3LYP/6-31G(d) basis set, where Becke's three-parameter hybrid exchange functional was combined with the Lee-Yang-Parr correlation functional¹ and a def2-SV(P) basis set.² The molecular properties were then obtained based on the optimized structures. All calculations were performed using the TURBOMOLE 6.0 program.³

The solid-state fluorescence quantum yields were determined on an integrating sphere according to the method described by de Mello et al.⁴ A 325 nm CW light from a He-Cd laser was used for optical pumping. The studied sample was placed inside the integrating sphere, where light emission was redistributed isotropically over the interior surface of the sphere. An optical fiber collected the light from the sphere and directed it to an Ocean Optics (Ocean Optics, Inc.) USB2000 miniature fiber optics spectrometer. The number of emitted photons was obtained by integrating the measured PL signal over the emission wavelengths. The response of the fiber and spectrometer detector system was normalized using a calibrated light source.

A femtosecond Ti:sapphire oscillator was used as excitation laser source (200 fs pulse width and 76 MHz repetition rate). The second harmonic (400 nm) of the oscillator output at 800 nm was used for the PL measurement. Time-resolved PL measurements were carried out on a Hamamatsu model C4334 streak camera coupled to a spectrometer, with a time resolution of 20 ps. The PL signals were collected at the emission peaks and the laser energy level for excitation was 4.8 mW. Decay in the PL intensity (I) with time (t) was fitted by a single-exponential function $y = A_1 \cdot \exp(-x/t_1) + y_0$ or double-exponential function $y = A_1 \cdot \exp(-x/t_1) + A_2 \cdot \exp(-x/t_2) + y_0$.

HeLa cells were cultured in minimum essential medium (MEM) containing 10%

fetal bovine serum (FBS) and antibiotics (100 units/mL penicillin and 100 µg/mL streptomycin) in a 5% humidity incubator at 37 °C. The HeLa cells were grown overnight on a cover slid in a 35 mm Petri dish. A DMSO solution of TPEB with a concentration of 5 mg/mL was prepared and then diluted by 1000 times by adding 2 µM of the solution into 2 mL aqueous buffer solution (MEM medium containing 10% FPS). The living cells were stained with such medium for 5 h. The cells were imaged on a fluorescent microscope (Olympus BX41) at blue light excitation = 460–490 nm (the green fluorescent signal was separated by a 505 nm long-pass dichroic mirror) or green light excitation = 510–550 nm (the red fluorescent signal is separated through a 570 nm long-pass dichroic mirror).

Preparation of Aggregates

Stock THF solutions of TPB, TPVB and TPEB with a concentration of 0.1 mM were prepared. An aliquot (1 mL) of these stock solutions was transferred to a 10 mL volumetric flask. After adding an appropriate amount of THF, water was added dropwise under vigorous stirring to furnish 10 µM THF/water mixtures with water fractions (f_w) of 0–90 vol %. Absorption and emission spectra of the resulting mixtures were measured immediately.

Synthesis

TPE-containing precursors **1–3**⁵ and BODIPY precursors **4–6**⁶ were synthesized according to our previously published paper.

8-[4'-(1,2,2-Triphenylvinyl)biphenyl-4-yl]-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (TPB). Into a 25 mL two-necked round-bottom flask were added 109 mg (0.31 mmol) of **4**, 118 mg (0.31 mmol) of **1**, 16.4 mg (0.014 mmol) of Pd(PPh₃)₄, 552 mg (4.00 mmol) of K₂CO₃ and a solvent mixture of THF/H₂O (6 mL/2 mL) in an atmosphere of nitrogen. The mixtures were stirred at 70 °C for 48 h under nitrogen. The reaction was quenched by adding 20 mL of saturated aqueous NH₄Cl solution. The aqueous phase was extracted with 60 mL of chloroform three times. The solvent was removed under reduced pressure and the crude product was purified on a silica-gel column using hexane as eluent. A dark red powder was obtained in 40% yield. IR (KBr), ν (cm⁻¹): 3060, 3029, 2924, 1556, 1413, 1387, 1260, 1114, 1079, 983,

913, 741, 699. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.95 (s, 2H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.11 (m, 17H), 6.78 (s, 2H), 6.54 (s, 2H). ^{11}B NMR (128 MHz, CDCl_3), δ (ppm): 0.35. ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 143.33, 142.97, 142.93, 142.90, 142.65, 140.96, 139.60, 136.65, 134.22, 131.93, 131.42, 130.74, 130.71, 130.67, 130.46, 127.16, 127.12, 127.03, 126.17, 125.96, 125.92, 125.65. ^{19}F NMR (376 MHz, CDCl_3), δ (ppm): -145.08. HRMS (MALDI-TOF): m/z 598.2388 (M^+ , calcd 598.2392).

(E)-8-{4-[4-(1,2,2-Triphenylvinyl)styryl]phenyl}-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (TPVB). Into a 50 mL two-necked round-bottom flask with a reflux condenser were placed 300 mg (1.02 mmol) of **5**, 630 mg (1.53 mmol) of **2**, 325 mg (1.53 mmol) of K_3PO_4 and 12 mg (0.05 mmol) of $\text{Pd}(\text{OAc})_2$. The flask was evacuated under vacuum and flushed with dry nitrogen three times. 10 mL of DMAC was then added to dissolve the reactants. The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into 100 mL water and extracted with 300 mL DCM three times. The organic extract was combined, washed with brine and dried over MgSO_4 . After filtration and solvent evaporation, the crude product was purified on a silica-gel column using hexane/DCM (10/1 v/v) as eluent. A red solid was obtained in 21% yield. IR (KBr), ν (cm^{-1}): 3022, 2950, 1563, 1539, 1412, 1387, 1261, 1117, 1077, 982, 913, 699. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.94 (s, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.10 (m, 19 H), 6.99 (d, $J = 4.0$ Hz, 2H), 6.56 (d, $J = 4.0$ Hz, 2H). ^{11}B NMR (128 MHz, CDCl_3), δ (ppm): 0.35. ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 144.02, 143.85, 143.65, 143.59, 143.53, 141.42, 140.40, 140.26, 134.76, 134.67, 132.75, 131.83, 131.38, 131.34, 131.31, 131.15, 130.87, 127.78, 127.73, 127.64, 126.88, 126.56, 126.51, 126.32, 126.14, 118.43. ^{19}F NMR (376 MHz, CDCl_3), δ (ppm): -145.08. HRMS (MALDI-TOF): m/z 624.2548 (M^+ , calcd 624.2593).

8-(4-{2-[4-(1,2,2-triphenylvinyl)phenyl]ethynyl}phenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (TPEB). Into a 25 mL round-bottom flask were added 105 mg (0.27 mmol) of **6**, 105.5 mg (0.30 mmol) of **3**, 4.2 mg (0.006 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 2.4

mg (0.012 mmol) of *t*-Bu₃P and 2.1 mg (0.01 mmol) of CuI. A solvent mixture of THF/Et₃N/DMF (2 mL/1 mL/0.5 mL) was then added to dissolve the reactants. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 5 h and was then poured into 10 mL of 0.1 M aqueous HCl solution. The mixture was extracted with 50 mL diethyl ether three times. The organic layers were combined and washed with concentrated aqueous NaHCO₃ solution and water. The organic phase was dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the crude product was purified on a silica-gel column using hexane as eluent. A dark red solid of TPEB was obtained in 34% yield. IR (KBr), ν (cm⁻¹): 3021, 2210, 1561, 1533, 1414, 1387, 1259, 1111, 1079, 982, 912, 700. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.95 (s, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.13 (m, 9H), 7.04 (m, 8H), 6.95 (d, *J* = 4.0 Hz, 2H), 6.56 (d, *J* = 4.0 Hz, 2H). ¹¹B NMR (128 MHz, CDCl₃), δ (ppm): 0.33. ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 144.63, 144.29, 143.39, 143.26, 141.94, 140.13, 134.74, 133.35, 131.49, 131.36, 131.33, 131.27, 131.10, 130.55, 127.85, 127.79, 127.68, 126.74, 126.67, 126.28, 120.40, 118.67, 92.57, 88.56. ¹⁹F NMR (376 MHz, CDCl₃), δ (ppm): -145.06. HRMS (MALDI-TOF): *m/z* 622.2379 (M⁺, calcd 622.2392).

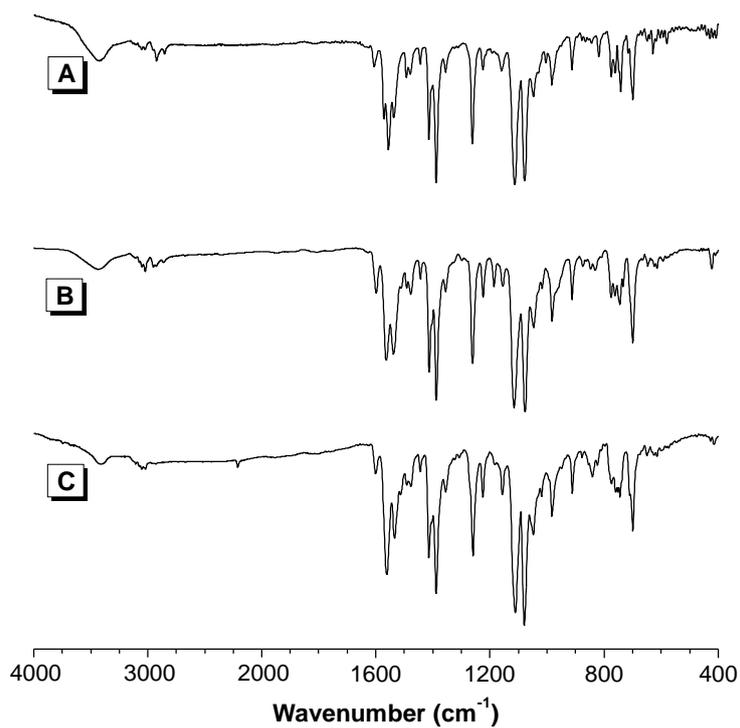


Fig. S1 IR spectra of (A) TPB, (B) TPVB and (C) TPEB.

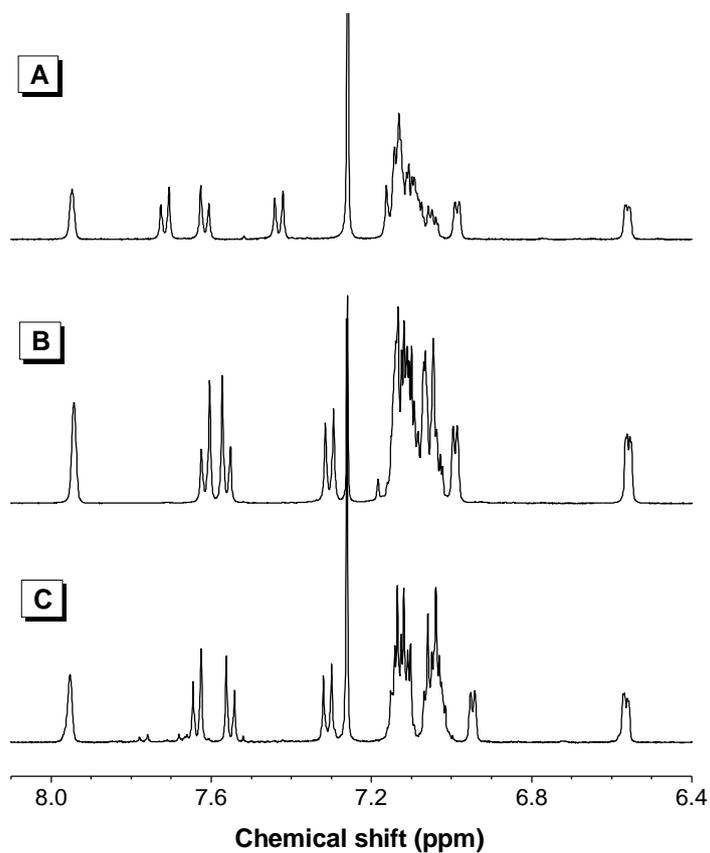


Fig. S2 ¹H NMR spectra of (A) TPB, (B) TPVB and (C) TPEB in CDCl₃.

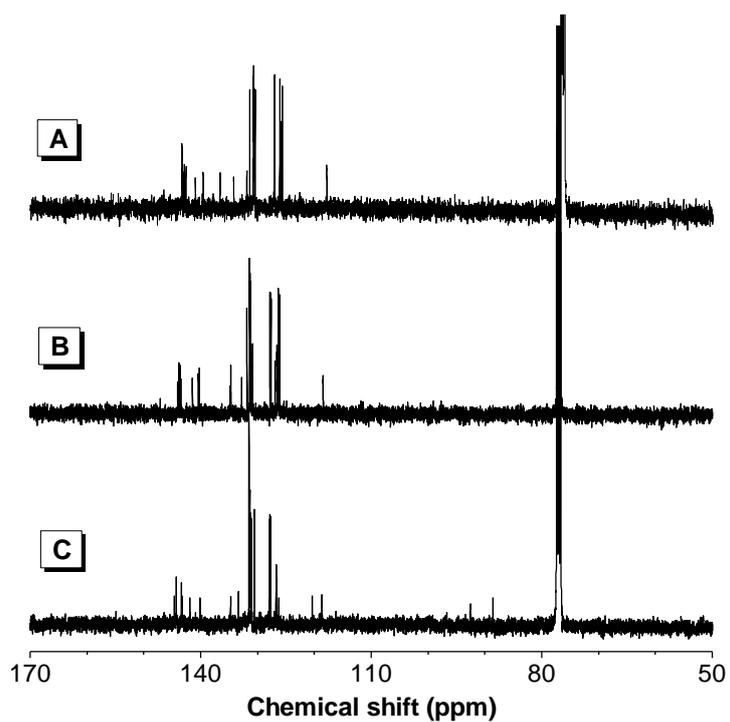


Fig. S3 ^{13}C NMR spectra of (A) TPB, (B) TPVB and (C) TPEB in CDCl_3 .

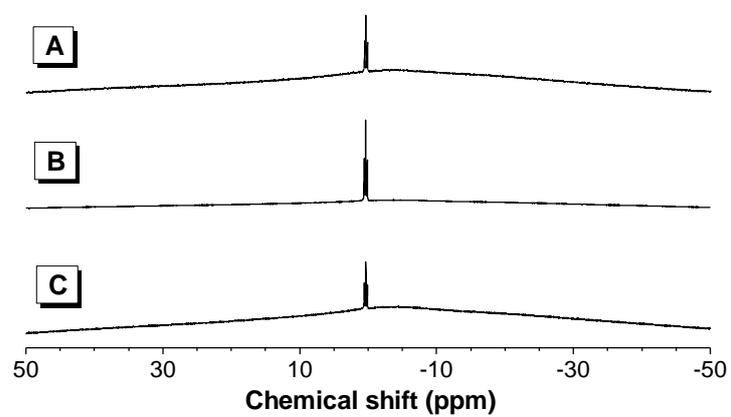


Fig. S4 ^{11}B NMR spectra of (A) TPB, (B) TPVB and (C) TPEB in CDCl_3 .

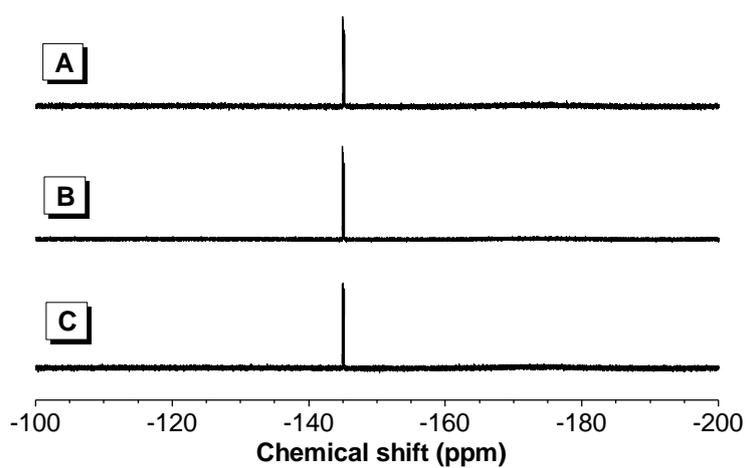


Fig. S5 ^{19}F NMR spectra of (A) TPB, (B) TPVB and (C) TPEB in CDCl_3 .

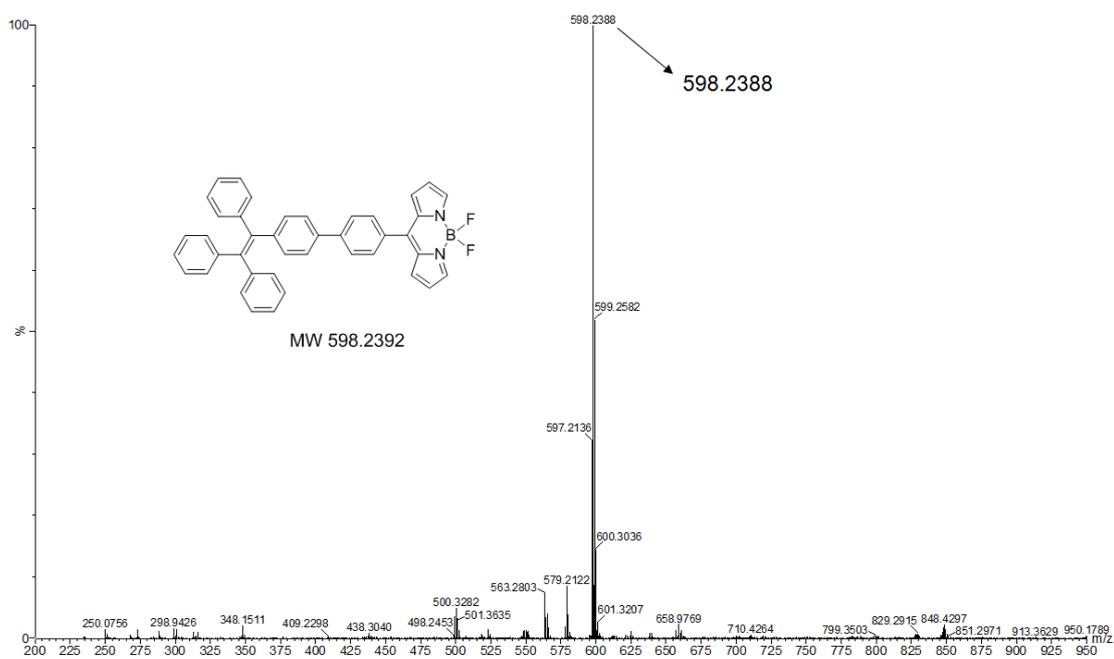


Fig. S6 HRMS spectrum of TPB.

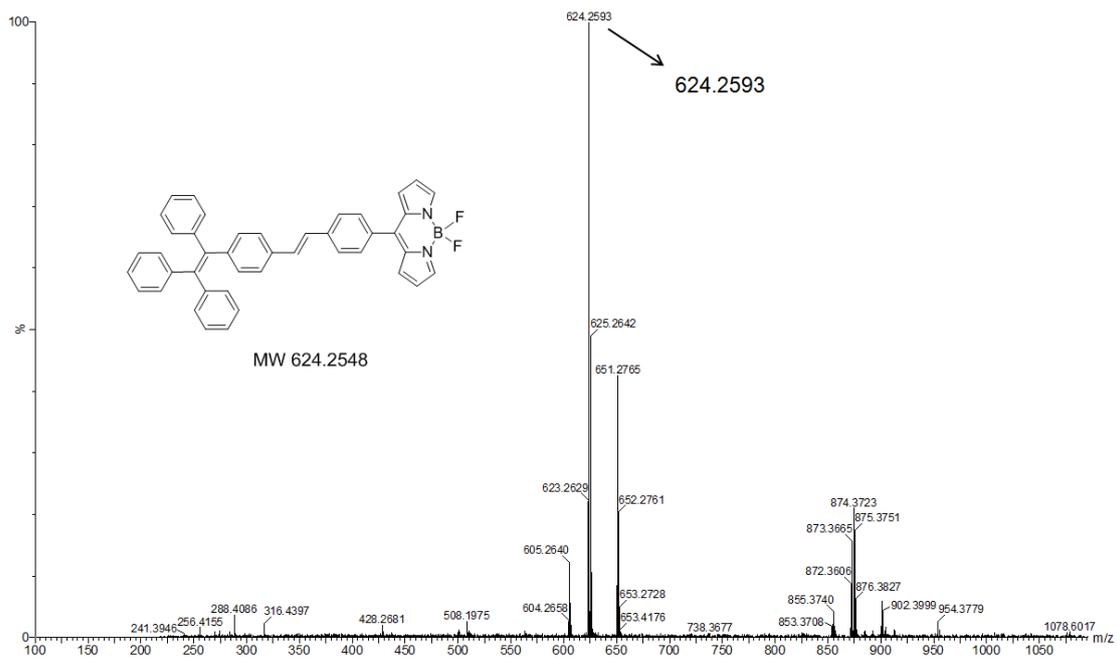


Fig. S7 HRMS spectrum of TPVB.

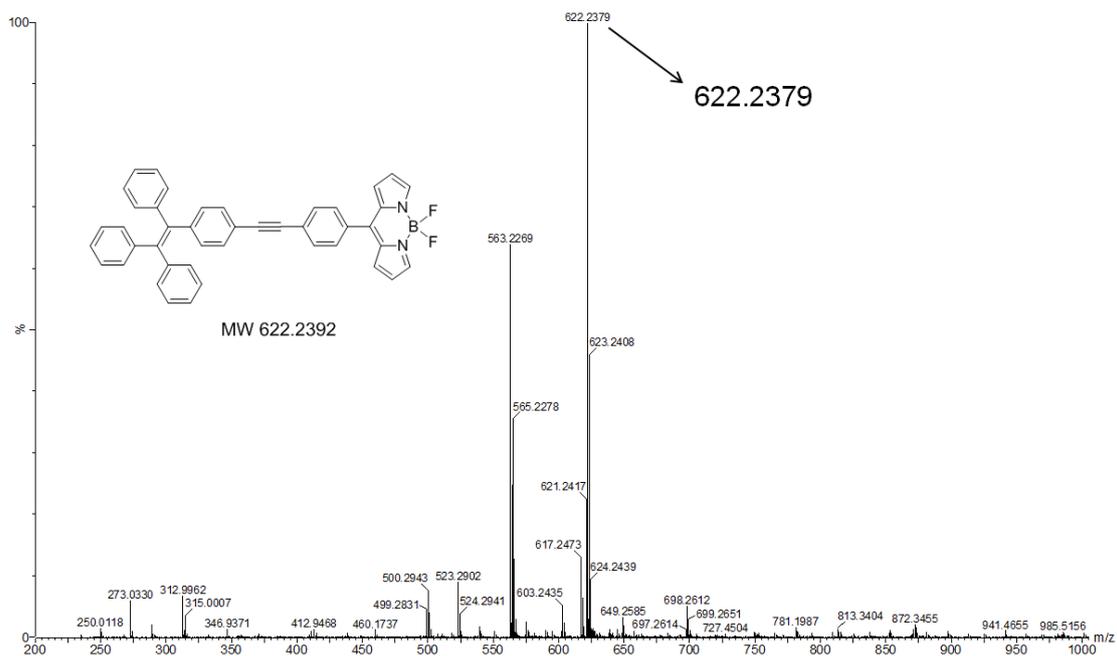


Fig. S8 HRMS spectrum of TPEB.

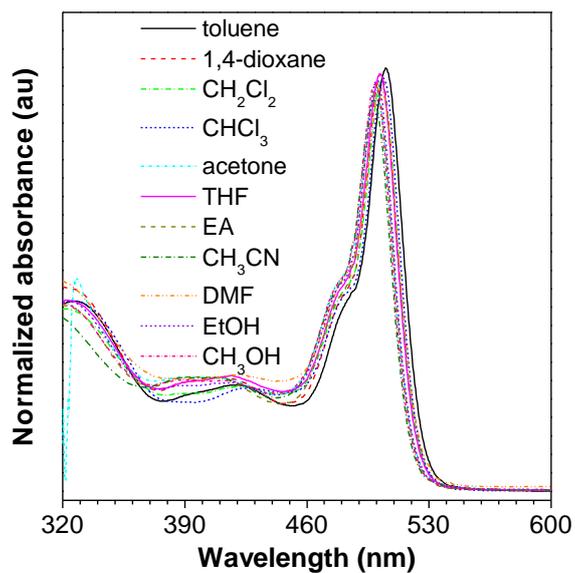


Fig. S9 UV spectra of TPB in different solvents. Concentration: 10 μ M.

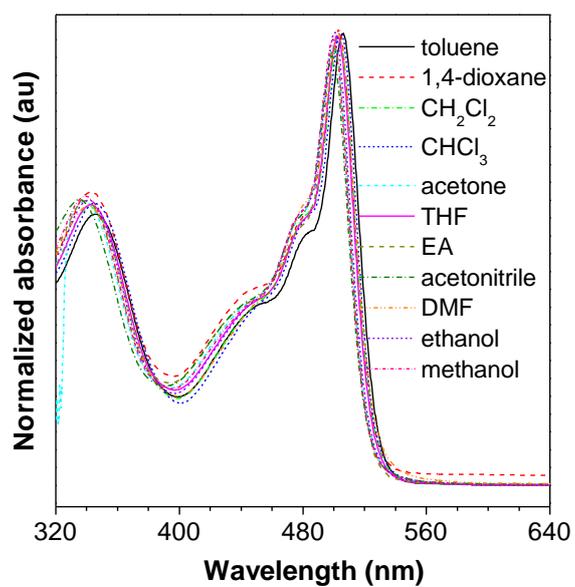


Fig. S10 UV spectra of TPVB in different solvents. Concentration: 10 μ M.

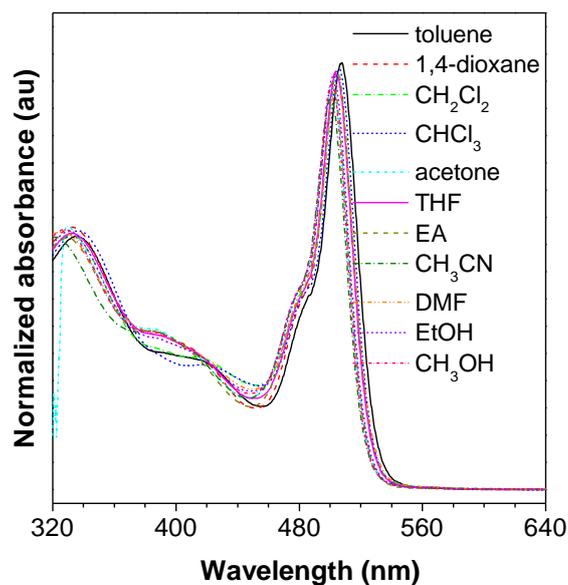


Fig. S11 UV spectra of TPEB in different solvents. Concentration: 10 μ M.

Table S1. Fluorescence quantum yields of TPB, TPVB and TPEB^a

Compd	Φ_{soln} (%)	Φ_{solid} (%)
TPB	0.2	5.0
TPVB	0.3	27.0
TPEB	0.1	7.5

^aAbbreviation: Φ_{soln} = fluorescence quantum yield in THF solution estimated using Rhodamine B as standard ($\Phi_{\text{F}} = 70\%$ in ethanol), Φ_{solid} = solid-state fluorescence quantum yield determined by an calibrated integrating sphere.

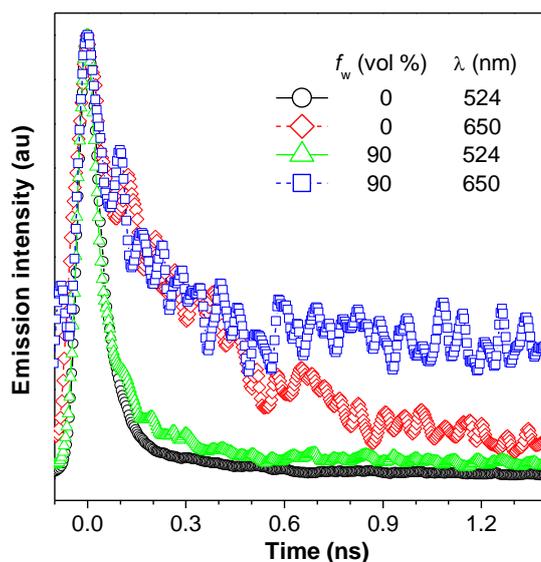


Fig. S12 Time-resolved fluorescence spectra of TPB in THF/water mixtures with different fractions of water (f_w). Solution concentration: 10 μ M; excitation wavelength: 400 nm.

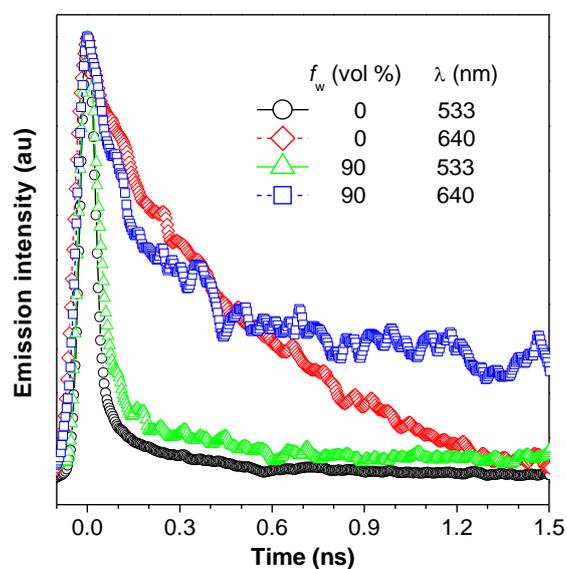


Fig. S13 Time-resolved fluorescence spectra of TPVB in THF/water mixtures with different fractions of water (f_w). Solution concentration: 10 μ M; excitation wavelength: 400 nm.

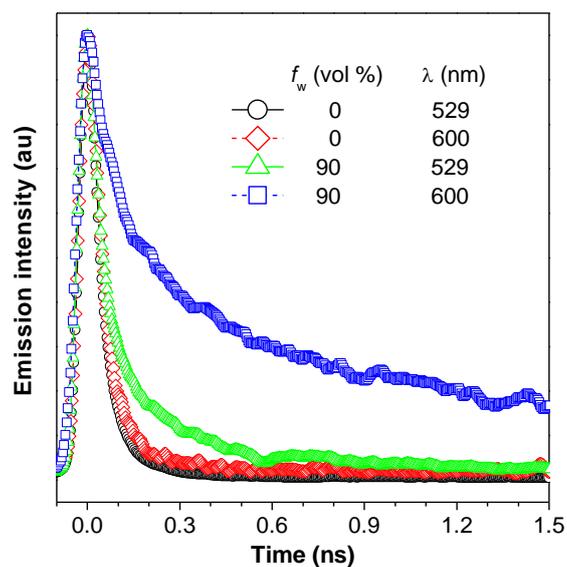


Fig. S14 Time-resolved fluorescence spectra of TPEB in THF/water mixtures with different fractions of water (f_w). Solution concentration: 10 μ M; excitation wavelength: 400 nm.

Table S2. Fluorescence decay parameters of TPB, TPVB and TPEB in THF solution and THF/water mixture^a

Compd	λ (nm)	THF				THF/water (1/9 v/v)			
		A_1/A_2	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle$ (ns)	A_1/A_2	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle$ (ns)
TPB	524	100/1	0.07		0.07	86/14	0.05	0.20	0.07
TPB	650	100/1	0.03		0.03	99/1	0.04	0.02	0.04
TPVB	533	100/1	0.02		0.02	88/12	0.04	0.37	0.08
TPVB	640	93/7	0.07	0.67	0.11	90/10	0.13	0.45	0.16
TPEB	529	100/1	0.05		0.05	82/18	0.04	0.21	0.07
TPEB	600	100/1	0.06		0.06	96/4	0.09	0.75	0.12

^aDynamic parameters determined from $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + y_0$, where A_1/A_2 and τ_1/τ_2 are the fractions (A) and lifetimes (τ) of shorter (1) and longer (2)-lived species. The weighted mean lifetime $\langle\tau\rangle$ was calculated according to the equation: $\langle\tau\rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$. Solution concentration: 10 μ M; excitation wavelength: 400 nm.

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