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Electronic Supporting Information for:

Conjugates of Tetraphenylethene and Diketopyrrolopyrrole: Tuning the Emission Property with Phenyl Bridge

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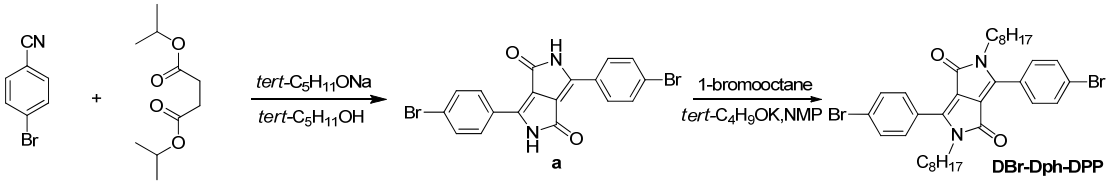
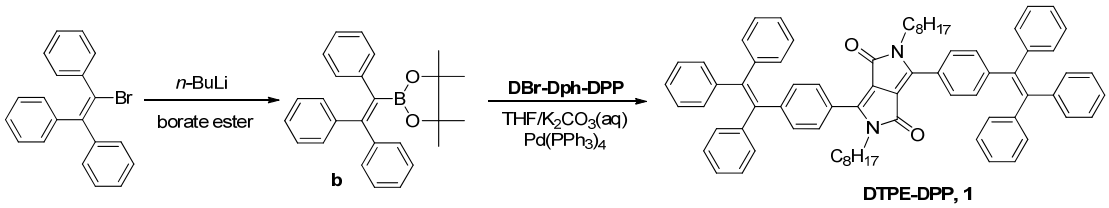
Experimental Section

Materials: 4-bromobenzophonene, diphenylmethane, magnesium and tertiary amyl alcohol were purchased from Alfa Aesar. 4-bromobenzonitrile and 2-isopropoxy-4,4,5,5-tetra- methyl-1,3,2-dioxa-borolane were purchased from Matrix. 4-bromo-benzophenone,4-*N,N*-dimethyl-amino-benzophenone, (2-bromoethene-1,1,2-triyl)tribenzene, 1-bromooctane, 4-bromo-*N,N*-di-methylaniline, diisopropyl succinate, $Pd(PPh_3)_4$, *N*-methyl pyrrolidone and *n*-BuLi were purchased from Acros. 4-bromobenzaldehyde and Dess-Martin periodinane were purchased from Energy chemical and used as received without further purification. Other reagents including *p*-toluene-sulfonic acid (TsOH), magnesium, benzophenone, Zinc dust, titanium tetrachloride, potassium tert-butoxide, diphenylmethane, ferric chloride, 4-bromo-benzophenone, potassium carbonate, magnesium sulfate, tertiary amyl alcohol, toluene, ethyl acetate and dichloromethane (DCM) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

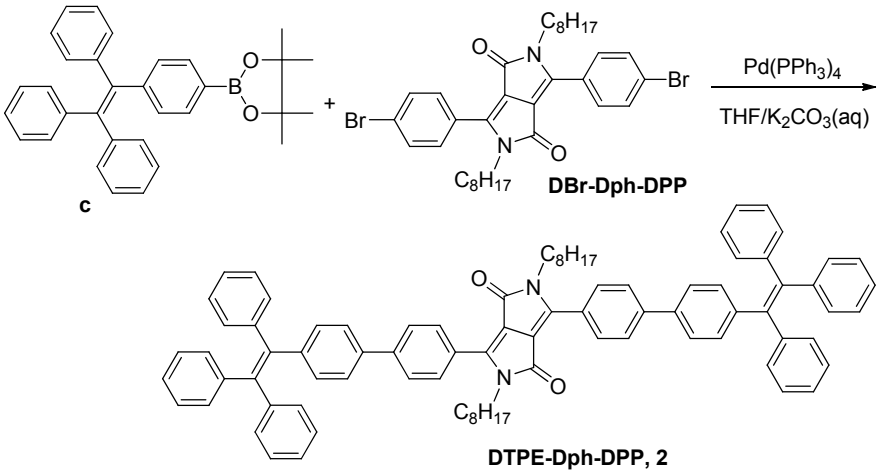
Instrumentation: ^{1}H and ^{13}C NMR spectra were measured on a Mercury plus 400 MHz NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS; δ = 0 ppm) as internal standard. Elemental analysis was performed on a ThermoFinnigan Flash EA1112 apparatus. UV absorption spectra were taken on a Varian CARY 100 Bio spectrophotometer. Fluorescence (FL) spectra were recorded on a spectrofluorophotometer (RF−5301PC, SHIMADZU, Japan). Scanning electron microscope (SEM) images were taken on a JSM-5510 (JEOL, Japan) scanning electron microscope. Fluorescent images were taken with a Zeiss Axiovert 200 inverted microscope equipped with a 100× oil immersion objective with a numerical aperture of 1.4 and an Ebq 100 Isolated electronic ballast for mercury vapour compressed-arc lamps. TGA spectra were recorded on a DSCQ 1000 (TA, USA) calorimeter. Φ_F values were estimated using Rhodamine B in ethanol (Φ_F = 70%) as standard. The absorbance of the solutions was kept between 0.04 and 0.06 to avoid the internal filter effect.



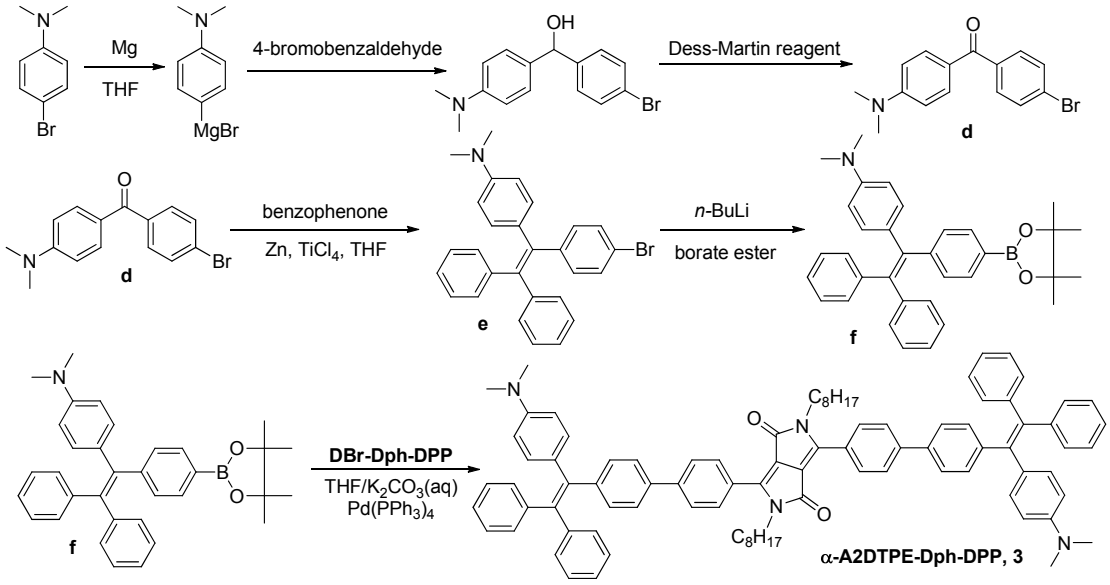
Scheme S1 Synthetic route to DBr-Dph-DPP.



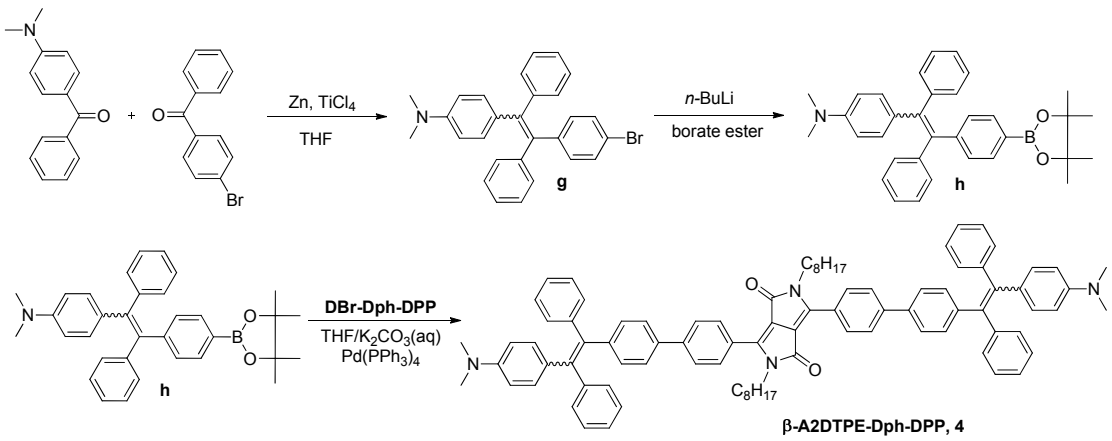
Scheme S2 Synthetic route to DTPE-DPP (molecule **1**).



Scheme S3 Synthetic route to DTPE-Dph-DPP (molecule **2**).



Scheme S4 Synthetic route to α-A2DTPE-Dph-DPP (molecule **3**).



Scheme S5 Synthetic route to β-A2DTPE-Dph-DPP (molecule **4**).

Synthesis of 4-Bromo-4'-N,N-dimethylaminobenzophenone (d): Magnesium (0.19 g, 8 mmol) and 4-bromo-*N,N*-dimethylaniline (1.8 g, 9 mmol) were added into a 100 mL two-necked round-bottomed flask under nitrogen. After injecting 10 mL distilled THF, the mixture was heated to reflux slowly until the magnesium is dissolved in THF totally. Then the mixture was cooled to 25 °C and waited for further use. In another 250 mL two-necked round-bottomed flask, 4-bromobenzaldehyde (1.3 g, 7 mmol) was added. The flask was then degassed and flushed with dry nitrogen three times, after which THF (30 mL) was injected. The mixture was cooled to 0 °C by an ice bath, the Grignard reagent prepared before was added drop by drop. After reaction at 25 °C for another 5 h, the reaction was quenched with a saturated ammonium chloride aqueous solution and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, 1.5eq of Dess-Martin periodinane (3.4 g, 8 mmol) and 40 mL of DCM were added. The reaction was tracked by TLC. After the reactants reacted totally, 20 mL of saturated sodium bicarbonate and saturated sodium thiosulfate aqueous solution (1:1 by volume) was put into the flask. The mixture was stirring at 25°C for 1~2 h, and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography, using petroleum ether/DCM/ethyl acetate (100:20:1 by volume) as eluent. The target compound (1.0 g) was obtained as a creamy solid in 64.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, 2H; Ar H), 7.60 (d, 4H, Ar H), 6.68 (d, 2H, Ar H), 3.08 (s, 6H; NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 194.54, 154.06, 138.71, 133.33, 131.94, 131.72, 126.49, 124.87, 111.25, 40.72.

Synthesis of 1-(4-bromophenyl)-1-(4-dimethylaminophenyl)-2,2-diphenylethene(e): Zinc dust (1.2 g, 18 mmol) was added into a 250 mL two-necked round-bottomed flask. The flask was degassed and flushed with dry nitrogen three times, after which THF (60 mL) was injected. The mixture was cooled to −5 to 0 °C by an ice-salt bath, then titanium tetrachloride (1 mL, 9 mmol) was added slowly. The mixture was allowed to warm to 25 °C and kept for 0.5 h and then refluxed at 74 °C for 2 h. The mixture was cooled to −5 to 0 °C again, treated with 0.5 mL of pyridine, and stirred for 10 min. Then a THF solution (10 mL) of benzophenone (0.58 g, 3.2 mmol) and compound d (0.8 g, 2.6 mmol) was added slowly. After refluxing overnight, the reaction was quenched with a 10% potassium carbonate aqueous solution and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and

solvent evaporation, the residue was purified by silica gel column chromatography, using petroleum ether/DCM/acetic ether (150:30:1 by volume) as eluent. The target compound (0.62 g) was obtained as a light yellow solid in 51.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.19 (d, 2H, Ar H), 7.12−7.05 (m, 8H; Ar H), 6.99 (t, 2H, Ar H), 6.91 (d, 2H, Ar H), 6.84 (d, 2H, Ar H), 6.46 (d, 2H, Ar H), 2.89 (s, 6H, NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.37, 144.13, 143.45, 133.20, 132.30, 131.38, 131.28, 130.66, 127.73, 127.71, 126.23, 126.15, 120.15, 111.55, 40.50.

Synthesis of 4-(1-(4-dimethylaminophenyl)-2,2-diphenylvinyl)phenylboronic acid, pinacol ester(f): *n*-BuLi (1.6 M in hexane, 0.9 mL, 1.4 mmol) was added dropwise into a THF solution (40 mL) of compound e (0.6 g, 1.32 mmol) at −78 °C under nitrogen. After the solution was stirred for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.4 mL, 2 mmol) was added into the solution slowly. Then the mixture was warmed to 25 °C. After being stirred for another 4 h, the mixture was quenched with saturated ammonium chloride solution and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography, using petroleum ether/ethyl acetate (30:1 by volume) as eluent. The target compound (0.44 g) was obtained as a light yellow solid in 67.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53 (d, 2H, Ar H), 7.18−6.90 (m, 12H; Ar H), 6.83 (d, 2H, Ar H), 6.45 (d, 2H, Ar H), 2.88 (s, 6H, NCH_3), 1.31 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.48, 144.47, 144.22, 140.96, 133.95, 132.37, 131.44, 131.39, 130.94, 127.67, 127.59, 126.07, 126.03, 111.34, 83.62, 40.44, 24.91.

Synthesis of 4-(2-(4-bromophenyl)-1,2-diphenylvinyl)-N,N-dimethylaniline(g): The compound was synthesized from Zinc dust (1.95 g, 30 mmol), titanium tetrachloride (1.7 mL, 15 mmol), 4-bromo-benzophenone (1.44 g, 5.5 mmol), 4-*N,N*-dimethylamino- benzophenone (1.13 g, 5 mmol) and distilled THF (60 mL). The procedure was similar to that used for the synthesis of 1-(4-bromophenyl)-1-(4-dimethylaminophenyl)-2,2-diphenylethene described above, the residue was purified by silica gel column chromatography, using petroleum ether/DCM (8:1 by volume) as eluent. And 1.0 g of target compound was obtained as a light yellow solid in 44.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24-7.16 (d, 2H, Ar H), 7.14−7.01 (m, 9H; Ar H), 6.99-6.92 (m, 2H, Ar H), 6.87-6.82 (m, 3H, Ar H), 6.49-6.42 (m, 2H, Ar H), 2.92-2.87 (d, 6H, NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 149.264, 144.395, 144.198, 143.824, 141.996, 137.887, 133.380, 132.554, 131.754, 131.693, 131.628, 131.096, 128.074, 127.957, 127.896, 126.609, 126.442, 111.670, 40.559.

Synthesis of 4-(1,2-diphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)vinyl)-N,N-dimethylaniline(h): Compound f was synthesized from *n*-BuLi (1.6 M in hexane, 0.9 mL, 1.4 mmol), compound g (0.6 g, 1.32 mmol), 2-isopropoxy-4,4,5,5- tetramethyl-1,3,2-dioxaborolane (0.4 mL, 2 mmol) and distilled THF (40 mL). The procedure was similar to that used for the synthesis of compound f described above, the residue was purified by silica gel column chromatography, using petroleum ether / DCM (5:1 by volume) as eluent. And 0.44 g of the target compound was obtained as a light yellow solid in 66.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49-7.43 (d, 2H, Ar H), 7.08−7.01 (m, 10H; Ar H), 7.01-6.88 (m, 2H, Ar H), 6.84-6.81 (m, 2H, Ar H), 6.43-6.41 (d, 2H, Ar H), 2.85-2.83 (d, 6H, NCH_3), 1.27-1.24 (d, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.742, 144.560, 144.270, 141.667, 138.774, 134.145, 133.855, 132.409,

131.541, 130.962, 128.937, 127.600, 127.558, 127.497, 126.333, 126.044, 111.258, 83.622, 40.831, 24.828.

Synthesis of 4,4,5,5-tetramethyl-2-(1,2,2-triphenylvinyl)-1,3,2-dioxaborolane(b): This compound was synthesized from *n*-BuLi (1.6 M in hexane, 9 mL, 15 mmol), (2-bromoethene-1,1,2-triyl)-tribenzene (2.01 g, 6 mmol), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (4.3 mL, 21.4 mmol) and distilled THF (40 mL). The procedure was similar to that used for the synthesis of compound f described above, the residue was purified by silica gel column chromatography, using petroleum ether / acetic ether (50:1 by volume) as eluent. And 1.8 g of the target compound was obtained as a white solid in 78.6% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36-7.33 (d, 2H, Ar H), 7.31−7.28 (t, 3H; Ar H), 7.15-7.10 (t, 2H, Ar H), 7.10-7.06 (t, 4H, Ar H), 7.06-7.01 (t, 2H, Ar H), 6.98-6.94 (t, 2H, Ar H), 1.12 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.498, 144.554, 141.950, 141.687, 130.919, 129.709, 129.415, 127.978, 127.942, 127.567, 127.513, 126.753, 125.840, 83.680, 24.542.

Synthesis of 3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(a): Sodium (0.44 g, 19 mmol) and ferric chloride (20 mg) was added into a 250 mL two-necked round-bottomed flask. The flask was degassed and flushed with dry nitrogen three times, after which 12 mL of distilled tertiary amyl alcohol was injected. The mixture was heated to reflux and then cooled to 50 °C until the sodium was dissolved totally. 4-bromobenzonitrile (1.73 g, 9.5 mmol) was added into the flask, and after which the mixture was heated to reflux again. Then a tertiary amyl alcohol solution (5 mL) of diisopropyl succinate (0.77 mL, 3.8 mol) was added in an hour. After refluxing for 24 h, 5 mL acetic acid was injected. The mixture was heated to 120 °C and refluxing for another hour. The precipitate was separated by filtration, and the filter cake was washed by hot water and methanol repeatedly. Compound a (1.8 g) was obtained as a red solid in 85% after drying. The crude product was used for the next step without further purification.

Synthesis of 3,6-bis(4-bromophenyl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DBr-Dph-DPP): Compound a (1.1 g, 2.3 mmol) and potassium *tert*-butoxide (1.3 g, 11.2 mmol) were added into a 250 mL twonecked round-bottomed flask under nitrogen. 40 mL of distilled NMP was injected and the mixture was stirred under 60% for 1 h. Then 1-bromooctane (2.4 mL, 13.8 mmol) was added slowly and the mixture was stirred under 60 °C for another 24 h. Then the mixture was cool to 25 °C and 40 mL toluene was then added and NMP was washed out by water. The collected organic layer was dried over anhydrous magnesium sulfate. After solvent evaporation, the crude product was purified by a silica gel column chromatography, using petroleum ether/ethyl acetate (100:1 by volume) as eluent. DBr-Dph-DPP (0.58 g) was obtained as an orange solid in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (q, 8H, Ar H), 3.71 (t, 4H, NCH_2), 1.54−1.50 (m, 4H, CH_2), 1.25−1.18 (m, 20H, CH_2), 0.85 (t, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.36, 147.43, 132.18, 130.11, 126.90, 125.80, 109.83, 41.77, 31.71, 29.35, 29.09, 28.97, 26.67, 22.61, 14.08. HRMS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{34}H_{42}Br_2N_2O_2$: 670.1593; found: 670.1594 (see Fig. S4). Anal.calcd. for $C_{34}H_{42}Br_2N_2O_2$: C, 60.90; H, 6.31; N, 4.18; found: C, 60.19; H, 6.62; N, 4.08.

Synthesis of 2,5-dioctyl-3,6-bis(4'-(1,2,2-triphenylvinyl)biphenyl-4-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DTPE-Dph-DPP, 2): TPE-containing precursor compound c was synthesized according to our previously published paper.[1] A mixture of compound c (0.30 g, 0.66 mmol),

DBr-Dph-DPP (0.20 g, 0.3 mmol), and $Pd(PPh_3)_4$ (20 mg, 2%) were added into a 100 mL two-necked round-bottomed flask. The flask was evacuated under vacuum and flushed with dry nitrogen three times. THF (10 mL) and potassium carbonate solution (2 M, 5 mL) were injected into the flask and the mixture was refluxed overnight. The solution was poured into water and extracted with DCM. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography, using chloroform/hexane (2:1 by volume) as eluent. Compound **2** (0.32 g) was obtained as a bright red solid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.90 (d, 4H, Ar H), 7.73 (d, 4H, Ar H), 7.43 (d, 4H, Ar H), 7.20−7.01 (m, 34H; Ar H), 3.81 (t, 4H, NCH_2), 1.64−1.60 (m, 4H, CH_2), 1.26−1.22 (m, 20H, CH_2), 0.85 (t, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.75, 147.89, 143.63, 143.53, 143.47, 143.12, 141.34, 140.20, 137.42, 131.86, 131.29, 131.23, 129.03, 127.69, 127.63, 127.55, 127.04, 126.76, 126.50, 126.45, 126.40, 126.14, 109.76, 41.95, 31.62, 29.36, 29.01, 28.92, 26.62, 24.70, 22.50, 14.00. HRMS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{86}H_{80}N_2O_2$: 1172.6220; found: 1172.6217 (see Fig. S5). Anal.calcd. for $C_{86}H_{80}N_2O_2$: C, 88.02; H, 6.87; N, 2.39; found: C, 87.81; H, 7.07; N, 2.39.

Synthesis of 3,6-bis(4'-(1-(4-(dimethylamino)phenyl)-2,2-diphenylvinyl)biphenyl-4-yl)-2,5-dioctyl-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (α-A2DTPE-Dph-DPP, 3): Compound 3 was synthesized from compound f (0.32 g, 0.65 mmol), DBr-Dph-DPP (0.20 g, 0.3 mmol), $Pd(PPh_3)_4$ (20 mg, 2% mmol)and distilled THF (10 mL). The procedure was similar to that used for the synthesis of DTPE-Dph-DPP described above, the residue was purified by silica gel column chromatography, using petroleum ether/DCM/acetic ether (40:10:1 by volume) as eluent. Finally, 0.24 g of compound **3** was obtained as a bright red solid in 63.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.91 (d, 4H, Ar H), 7.75 (d, 4H, Ar H), 7.44 (d, 4H, Ar H), 7.20−7.07 (m, 24H; Ar H), 6.94 (d, 4H, Ar H), 6.51 (d, 4H, Ar H),3.83 (t, 4H, NCH_2), 2.93 (s, 12H, NCH_3), 1.71−1.60 (m, 4H, CH_2), 1.31−1.19 (m, 20H, CH_2), 0.93-0.84 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.51, 149.59, 148.69, 145.23, 145.15, 145.02, 144.07, 141.16, 139.99, 137.95, 133.09, 132.90, 132.19, 132.10, 129.82, 128.39, 128.35, 127.80, 127.48, 126.78, 112.07, 110.52, 42.76, 41.03, 32.42, 30.17, 29.81, 29.71, 27.43, 23.28, 14.78. HRMS (MALDI-TOF, m/z): $[M+1]^+$ calcd for $C_{90}H_{90}N_4O_2$: 1259.7097; found: 1259.7094 (see Fig. S6). Anal.calcd. for $C_{90}H_{90}N_4O_2$: C, 85.81; H,7.20; N, 4.45; found: C, 85.49; H, 7.48; N, 4.46.

Synthesis of 2,5-dioctyl-3,6-bis(4-(1,2,2-triphenylvinyl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (DTPE-DPP, 1): DTPE-DPP was synthesized from compound b (0.251 g, 0.66 mmol), DBr-Dph-DPP (0.20 g, 0.3 mmol), $Pd(PPh_3)_4$ (20 mg, 2% mmol) and distilled THF (10 mL). The procedure was similar to that used for the synthesis of DTPE-Dph-DPP described above, the residue was purified by silica gel column chromatography, using petroleum ether/DCM/acetic ether (40:10:1 by volume) as eluent. And 0.21 g of compound **1** was obtained as an orange solid in 69.3% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.74-7.47 (d, 4H, Ar H), 7.39-6.84 (m, 34H, Ar H), 3.69 (s, 4H, NCH_2), 1.62−1.49 (m, 4H, CH_2), 1.35−1.09 (m, 20H, CH_2), 0.90 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 162.696, 147.855, 146.668, 143.304, 143.106, 142.314, 140.318, 131.612, 131.313, 131.253, 131.181, 127.865, 127.749, 127.698, 127.572, 126.625, 126.088, 109.466, 41.791, 31.642, 29.256, 29.067, 28.983, 26.657, 22.534, 14.034. Anal.calcd. for $C_{74}H_{72}N_2O_2$: C, 87.02; H, 7.11; N, 2.74; found: C, 86.62; H, 7.27; N, 2.77.

Synthesis of 2,5-dioctyl-3,6-bis(4-(1,2,2-triphenylvinyl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (β-A2DTPE-Dph-DPP, 4): Compound 4 was synthesized from compound h (0.20 g, 0.40 mmol), DBr-Dph-DPP (0.13 g, 0.2 mmol), $Pd(PPh_3)_4$ (20 mg, 2% mmol) and distilled THF (10 mL). The procedure was identical to that used for the synthesis of α-A2DTPE-Dph-DPP described above, the residue was purified by silica gel column chromatography, using petroleum ether/DCM/acetic ether (40:10:1 by volume) as eluent. And 0.14 g of compound **4** was obtained as a bright red solid in 54.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.02-7.82 (d, 4H, Ar H), 7.78-7.68 (d, 4H, Ar H), 7.47-7.36 (d, 4H, Ar H), 7.24−7.04 (m, 24H; Ar H), 7.01-6.82 (d, 4H, Ar H), 6.59-6.38 (d, 4H, Ar H),3.81 (t, 4H, NCH_2), 2.92 (s, 12H, NCH_3), 1.78−1.52 (m, 4H, CH_2), 1.37−1.09 (m, 20H, CH_2), 1.00-0.72 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.20, 148.41, 144.88, 144.51, 143.06, 141.87, 137.15, 132.68, 132.28, 131.80, 129.39, 128.09, 127.87, 127.76, 127.34, 127.05, 126.53, 126.39, 110.11, 42.21, 31.99, 29.96, 29.77, 29.38, 29.28, 27.01, 22.07.

Theoretical Calculation.

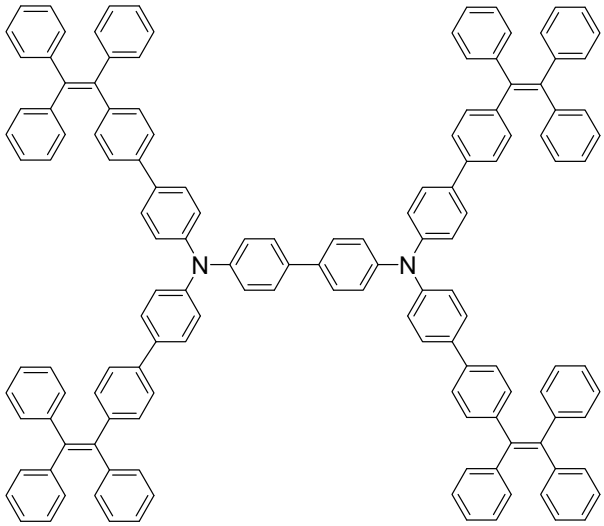
All calculations on the considered molecules were performed by using the Gaussian 09 program package.[2] B3lYP/6-31g (d) was employed to do the single point energy calculation based on the crystal structure. The relative energies of the HOMO and LUMO levels were obtained from the computed results.

The quenching factor (Φ_q) is calculated by using the equation of:

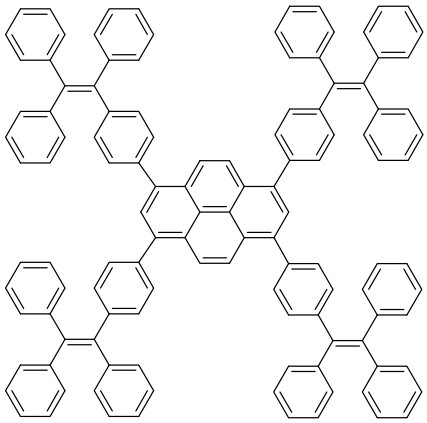
$\Phi_q = (\Phi_{solut} - \Phi_{solid})/\Phi_{solut}$

Where Φ_{solut} and Φ_{solid} are the emission quantum efficiencies of the luminogen in dilute solution and in solid film, respectively.

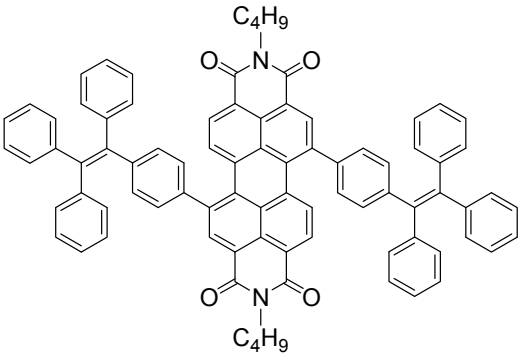
Chart S1 Chemical structures of the conjugates of TPE with classical organic dyes using triphenylamine, [3] pyrene [4] and perylenebisimde [5] as representatives. There is a common feature that the TPE moieties are directly attached to the central luminogens.



TPE-Triphenylamine conjugate

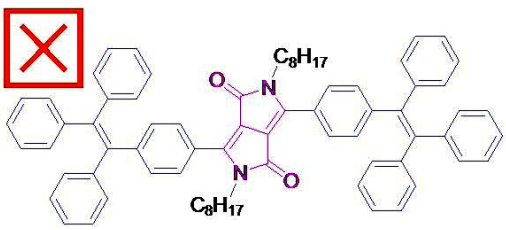


TPE-Pyrene conjugate

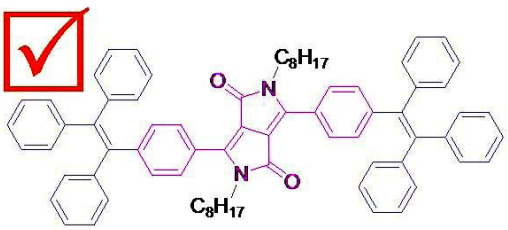


TPE-Perylene-bisimide conjugate

Chart S2



2TPE + DPP



Dph-DPP modified by α, β,β-triphenylethene

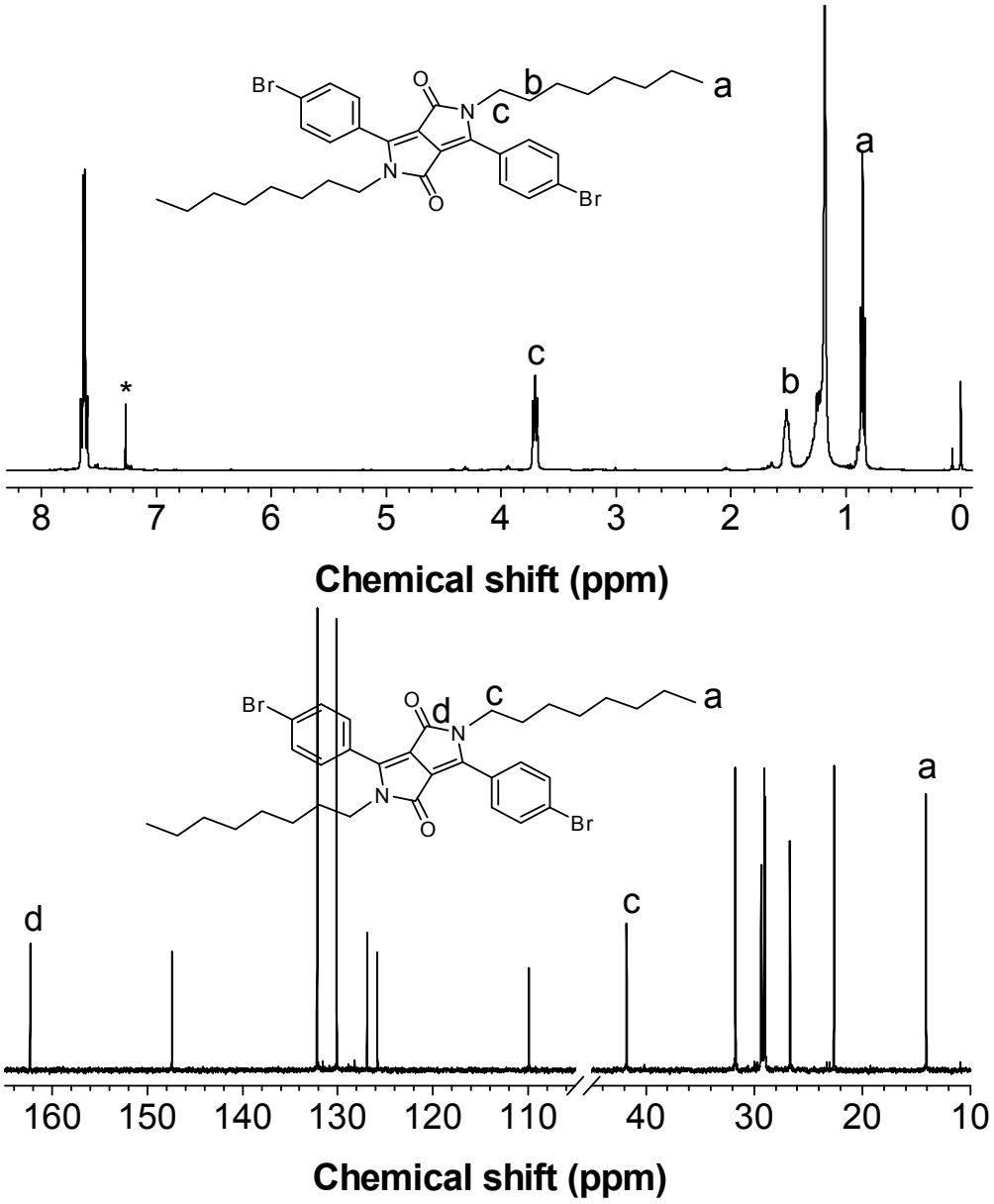


Fig. S1 ^{1}H NMR and ^{13}C NMR spectra of DBr-Dph-DPP in $CDCl_3$. The solvent peak is marked with asterisk.

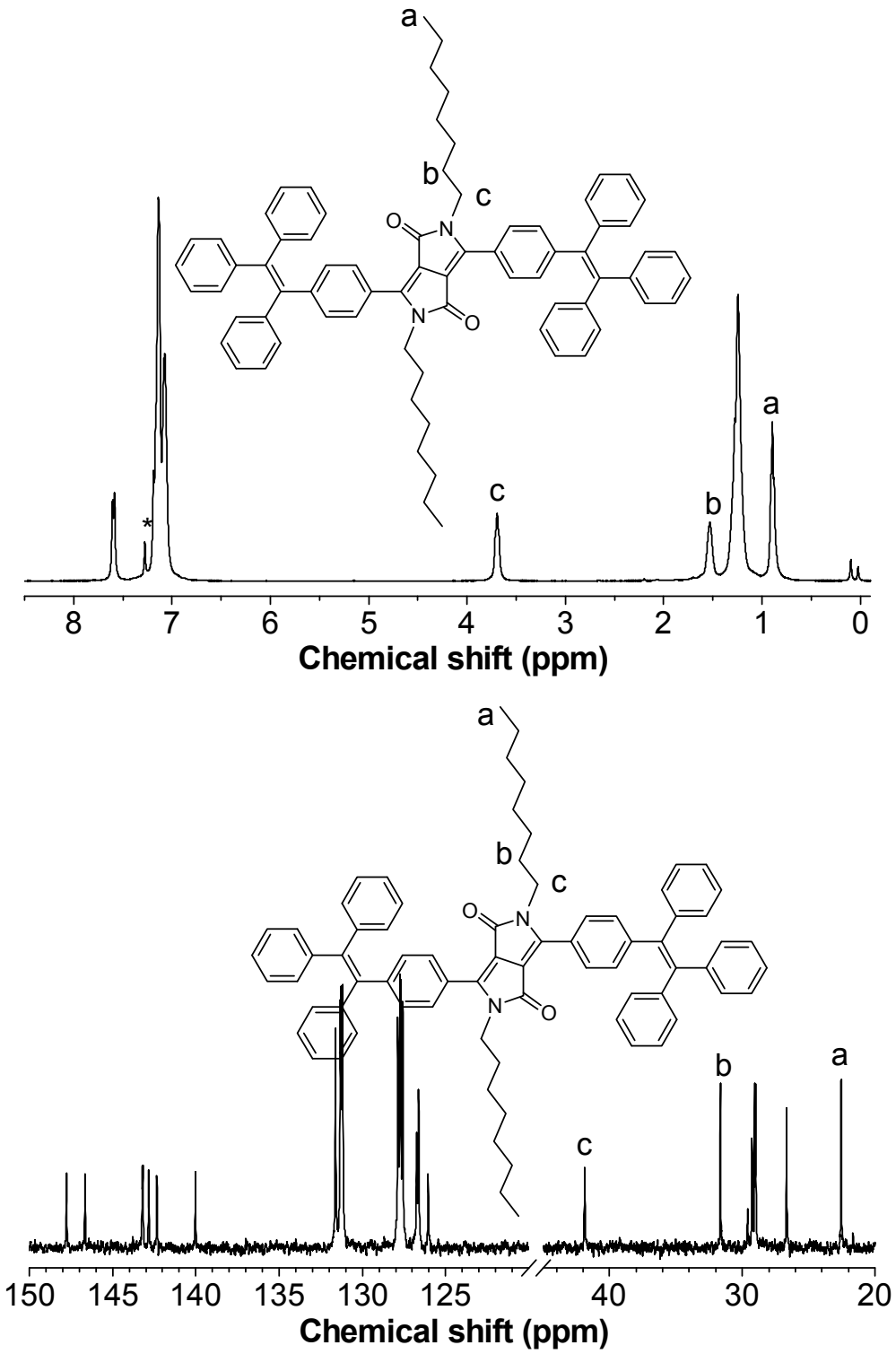


Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of DTPE-DPP (**1**) in $CDCl_3$. The solvent peak is marked with asterisk.

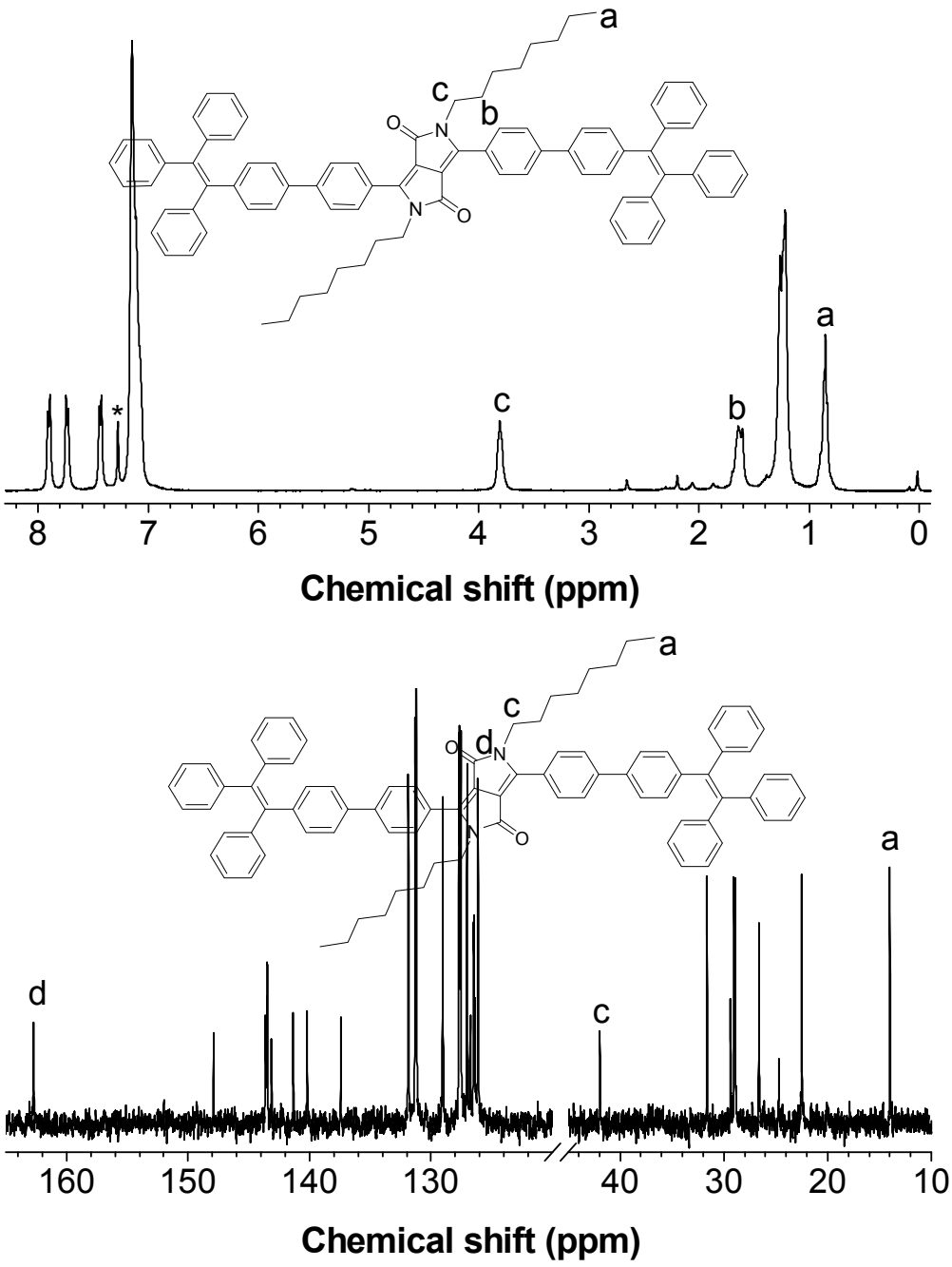


Fig. S3 ^{1}H NMR and ^{13}C NMR spectra of DTPE-Dph-DPP (**2**) in $CDCl_3$. The solvent peak is marked with asterisk.

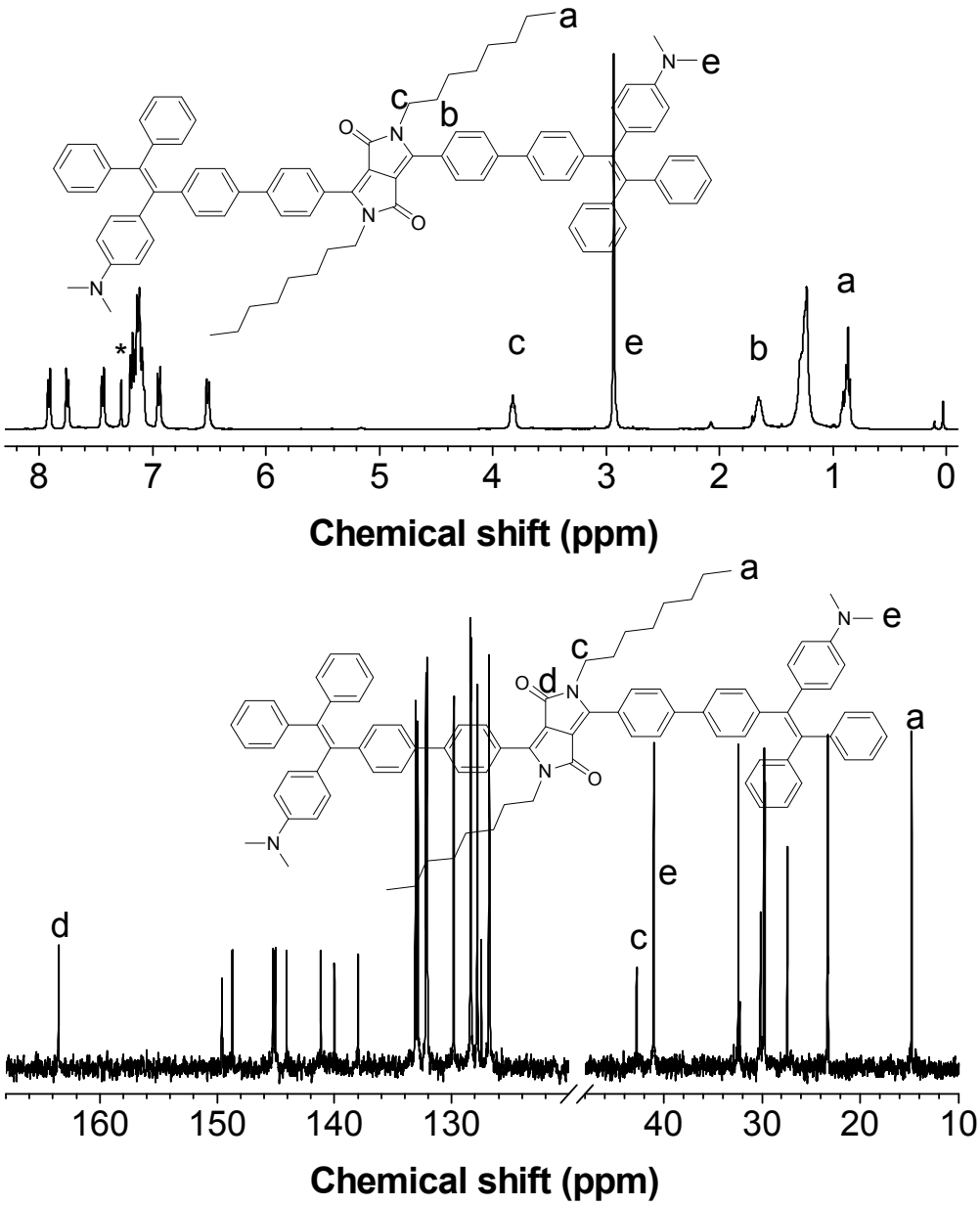


Fig. S4 ^{1}H NMR and ^{13}C NMR spectra of α-A2DTPE-Dph-DPP (**3**) in $CDCl_3$. The solvent peak is marked with asterisk.

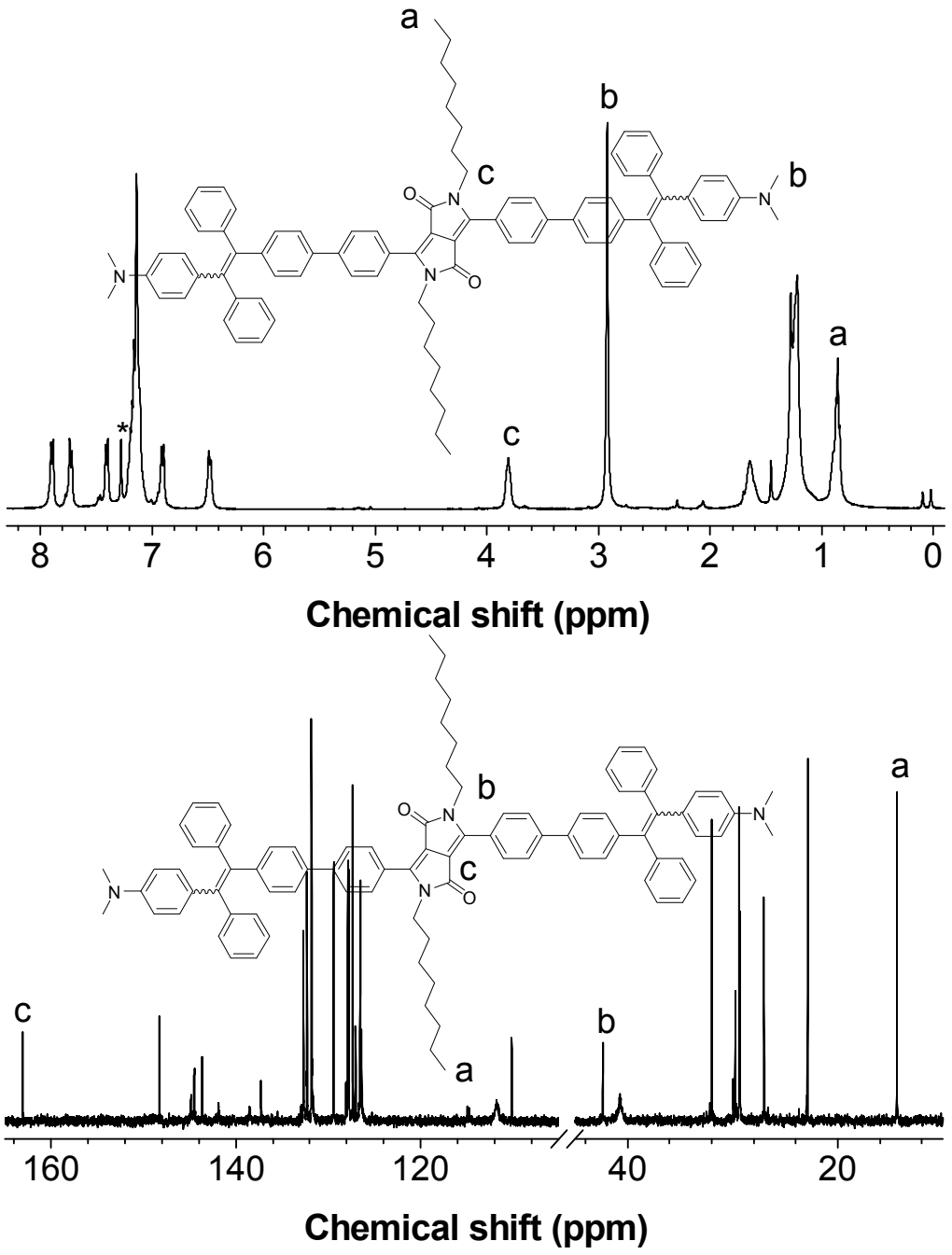


Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of β-A2DTPE-Dph-DPP (**4**) in $CDCl_3$. The solvent peak is marked with asterisk.

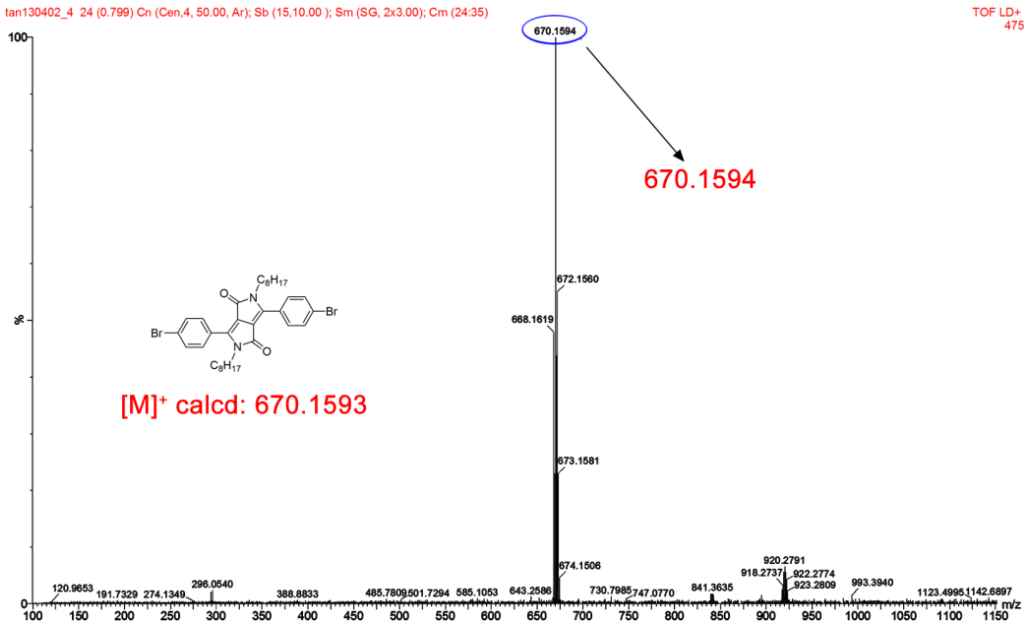


Fig. S6 MALDI-TOF mass spectrum of DBr-Dph-DPP.

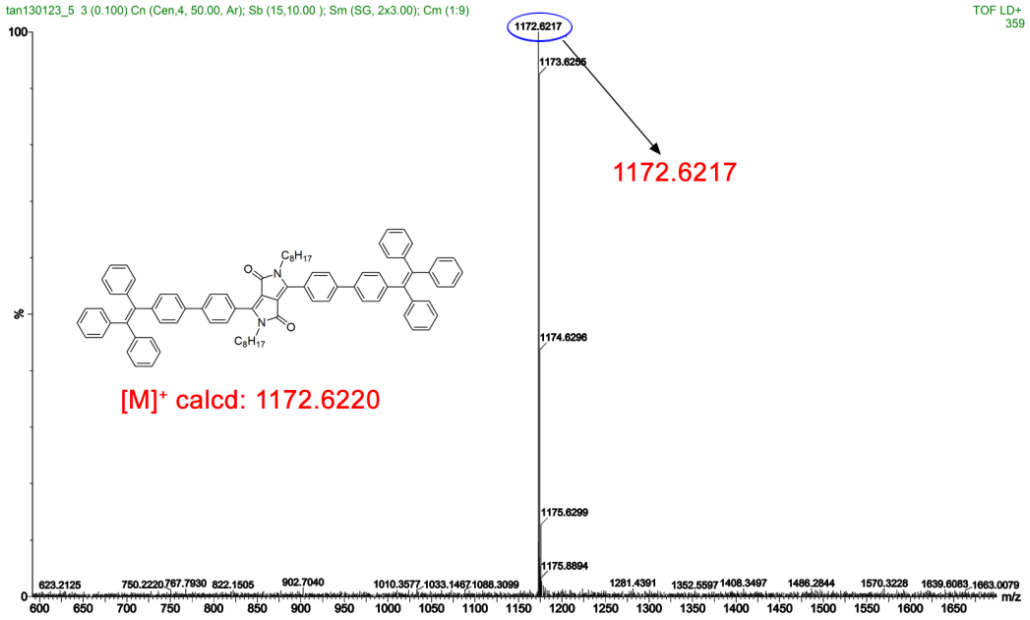


Fig. S7 MALDI-TOF mass spectrum of DTPE-Dph-DPP (**2**).

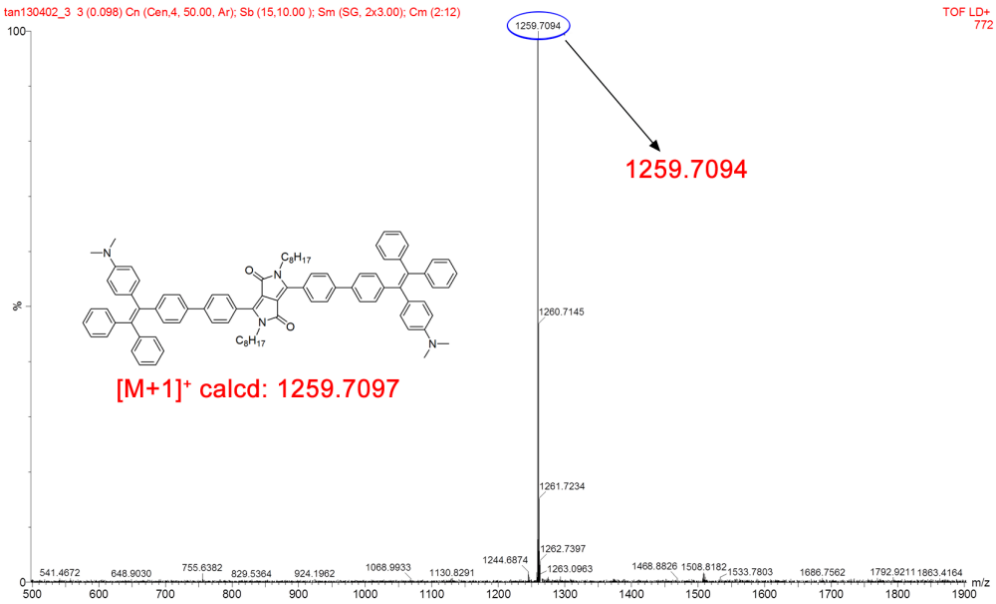


Fig. S8 MALDI-TOF mass spectrum of α-A2DTPE-Dph-DPP (**3**).

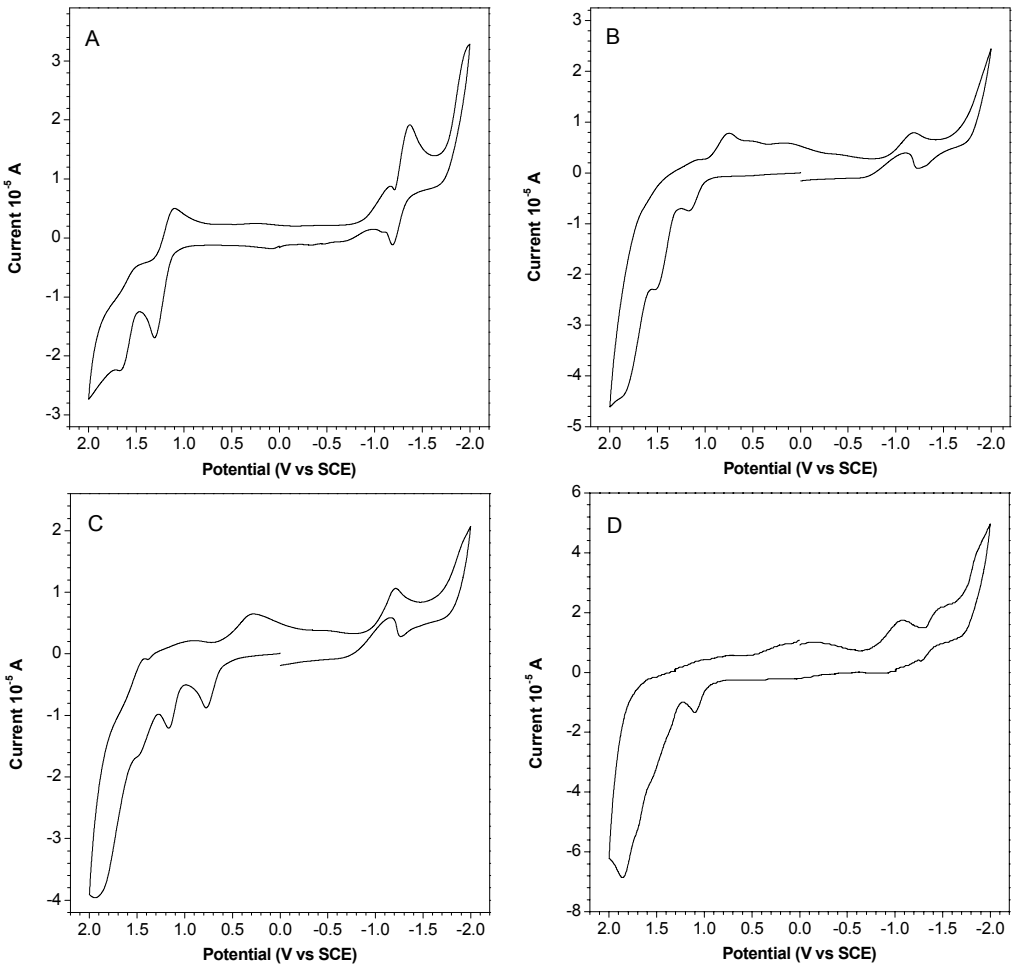


Fig. S9 The cyclic voltammograms of (A) DBr-Dph-DPP, (B) DTPE-Dph-DPP (**2**), (C) α-A2DTPE-Dph-DPP (**3**) and (D) DTPE-DPP (**1**) measured in dichloromethane containing 0.1M $[nBu4N]^{+}[PF6]^{-}$ at a scan rate of 50 mV/s.

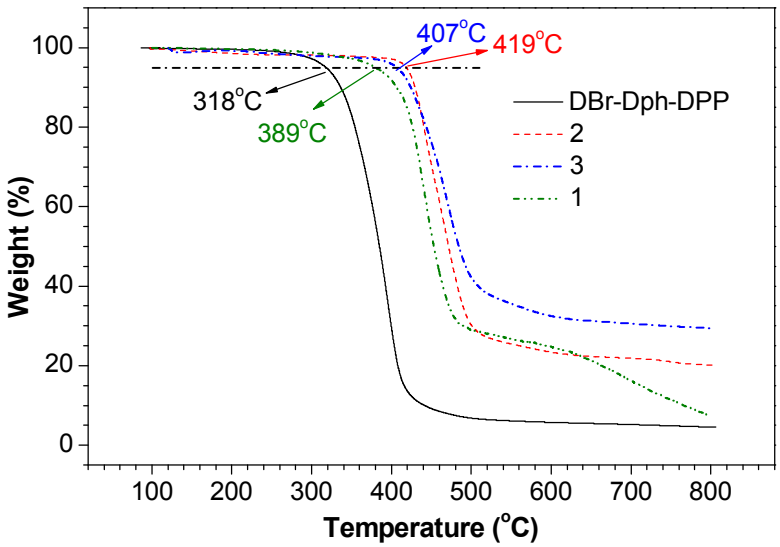


Fig. S10 TGA thermograms of DBr-Dph-DPP, DTPE-DPP (**1**), DTPE-Dph-DPP (**2**), and α-A2DTPE-Dph-DPP (**3**) recorded after pre-warming at 120 °C for 10 min under nitrogen at a heating rate of 10 °C min^{-1}.

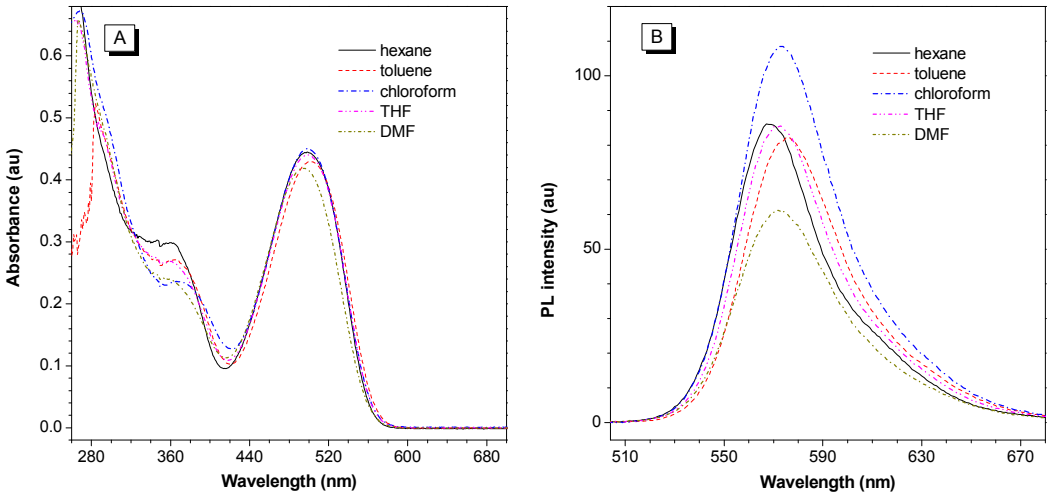
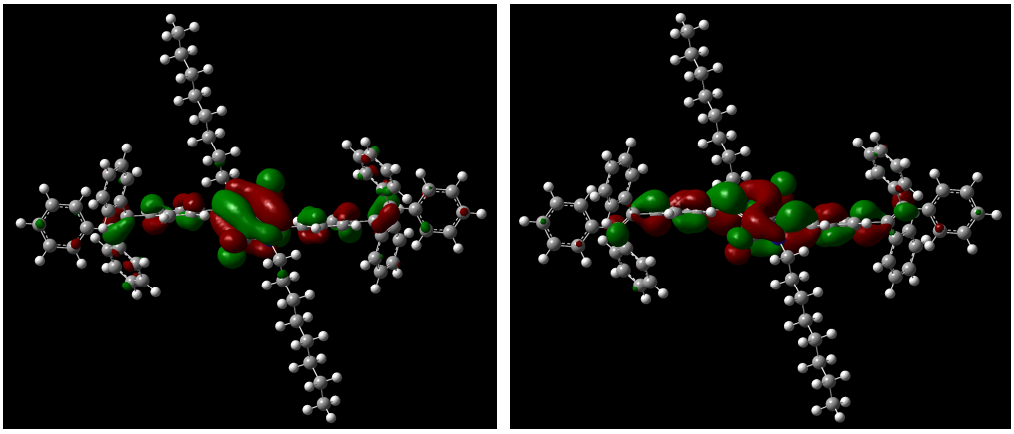


Fig. S11 (A) UV-visible absorption and (B) fluorescence (FL) spectra of DTPE-DPP (**1**) in different solvents. Concentration: 10 μM.



E_{LUMO} = -2.28 eV E_{HOMO} = -4.90 eV

Fig. S12 Molecular orbital amplitude plots of HOMO and LUMO energy levels of DTPE-DPP (**1**).

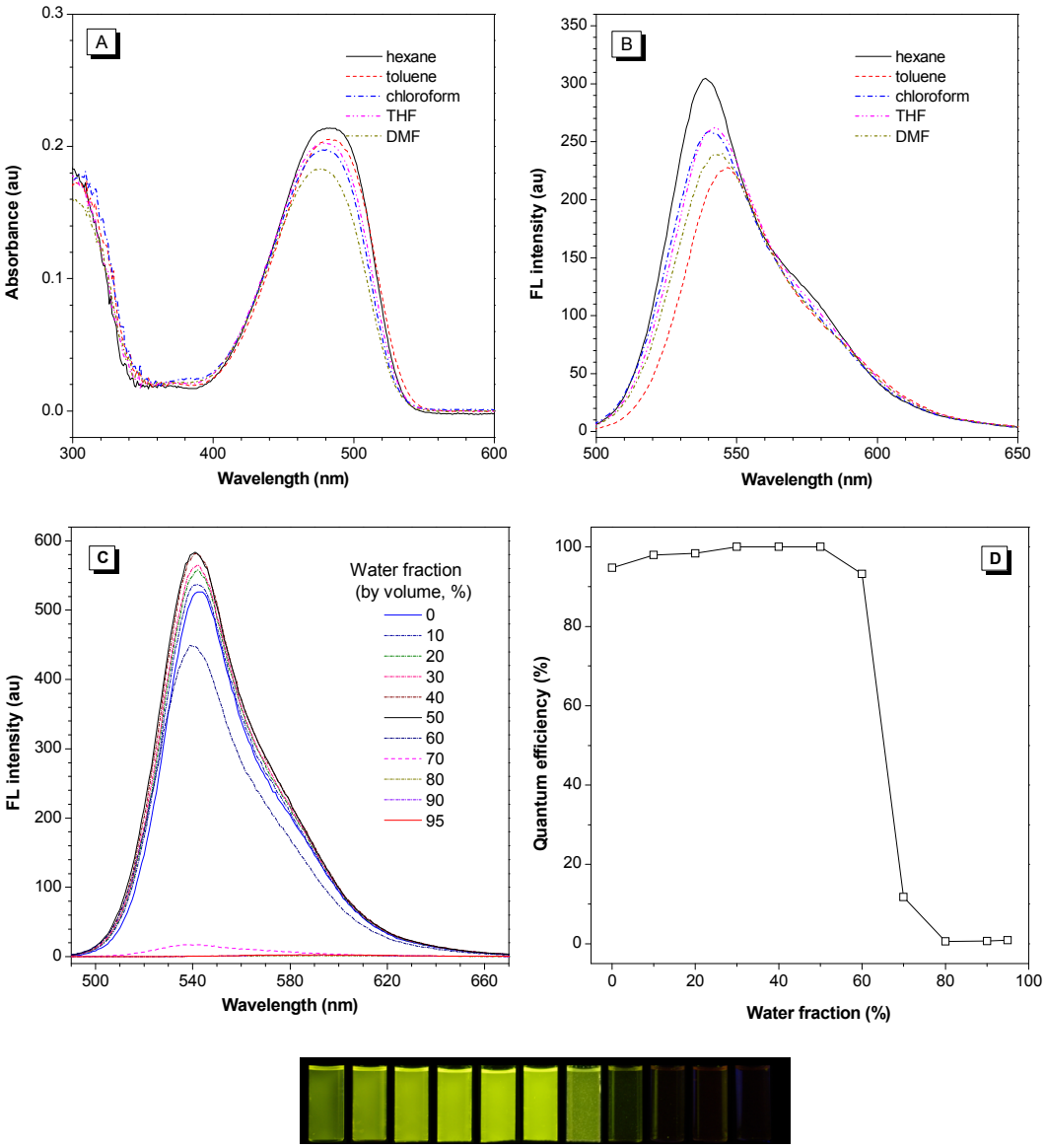


Fig. S13 (A) UV-visible and (B) fluorescence spectra of DBr-Dph-DPP in different solvents. (C) Change in fluorescence intensity and (D) quantum efficiency of DBr-Dph-DPP in THF/water mixtures with different water fraction (f_w). The lower panel shows the fluorescence photographs corresponding to the data in (D). Concentration: 10 μM; λ_{ex}: 365 nm.

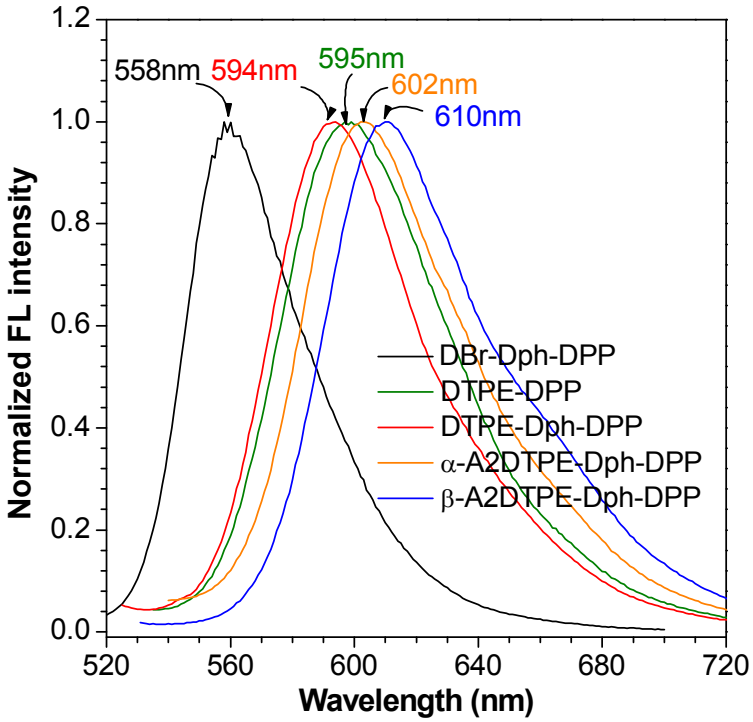


Fig. S14 Normalized fluorescent spectra of the solid films of DBr-Dph-DPP and molecule **1**, **2**, **3** and **4** cast on quartz plates and recorded by the excitation with their absorption maxima (λ_{abs}).

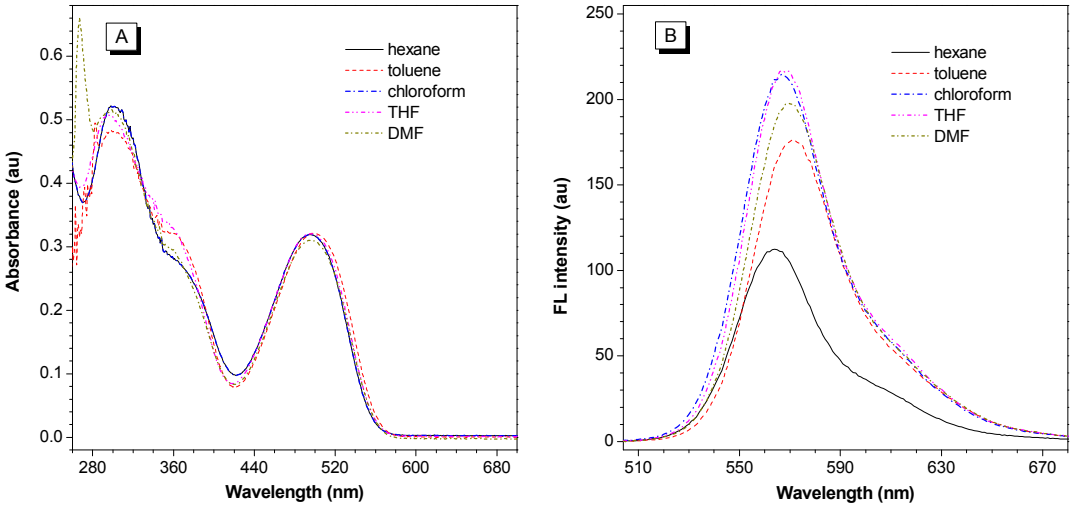


Fig. S15 (A) UV-visible absorption and (B) FL spectra of DTPE-Dph-DPP (**2**) in different solvents. Concentration: 10 μM.

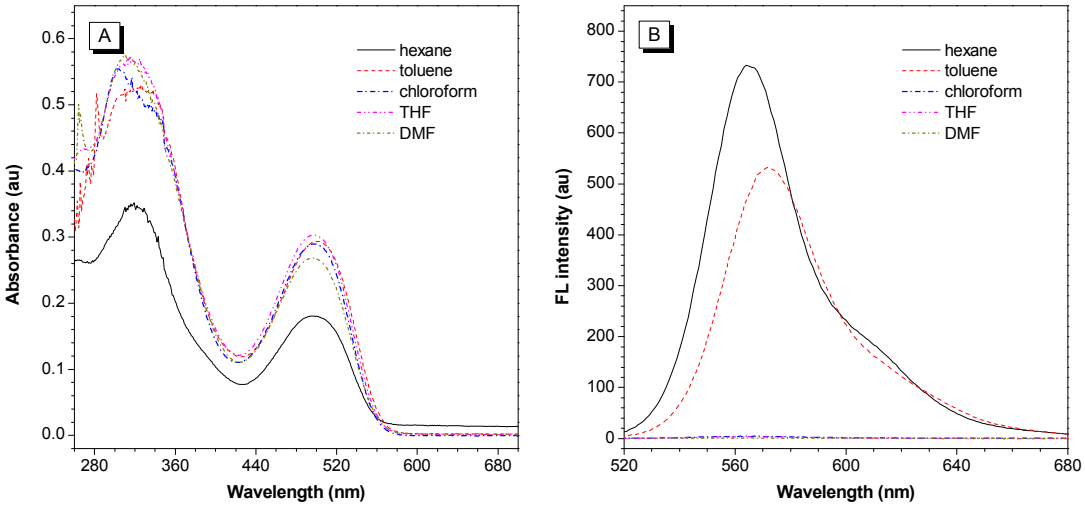


Fig. S16 (A) UV-visible absorption and (B) FL spectra of α-A2DTPE-Dph-DPP (**3**) in different solvents. Concentration: 10 μM.

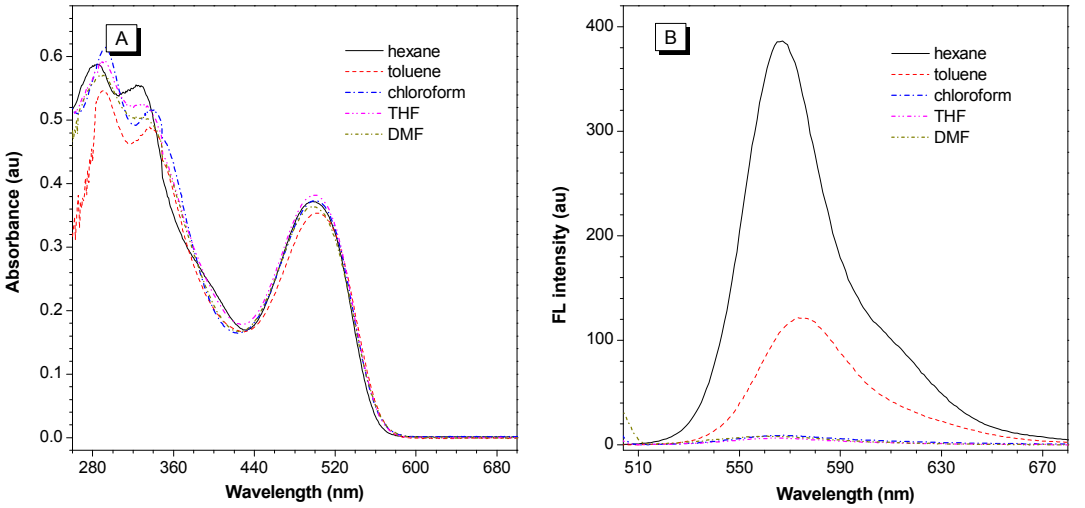


Fig. S17 (A) UV-visible absorption and (B) FL spectra of β-A2DTPE-Dph-DPP (**4**) in different solvents. Concentration: 10 μM.

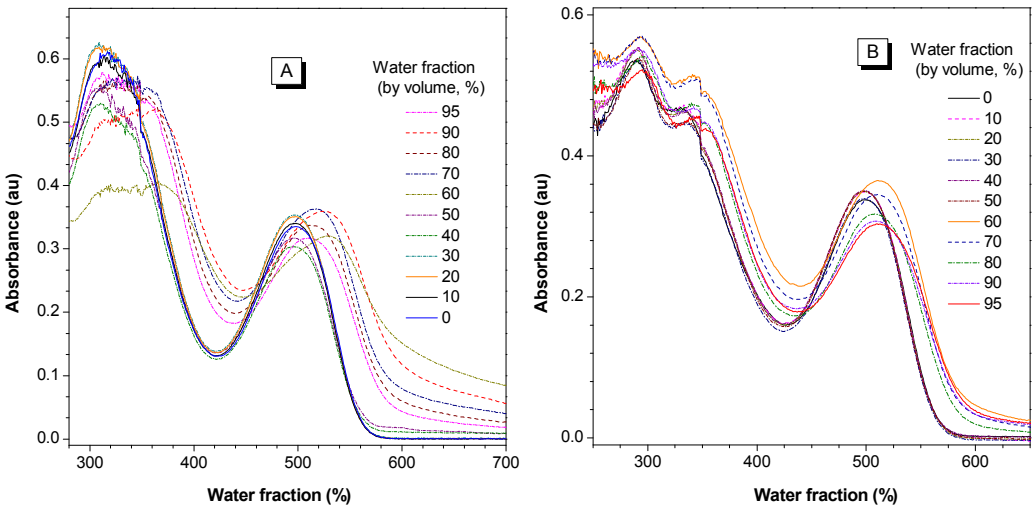


Fig. S18 (A) UV-visible absorption spectra of α-A2DTPE-Dph-DPP (**3**) and (B) β-A2DTPE-Dph-DPP (**4**) in THF/water mixtures with different f_w. Concentration: 10 μM.

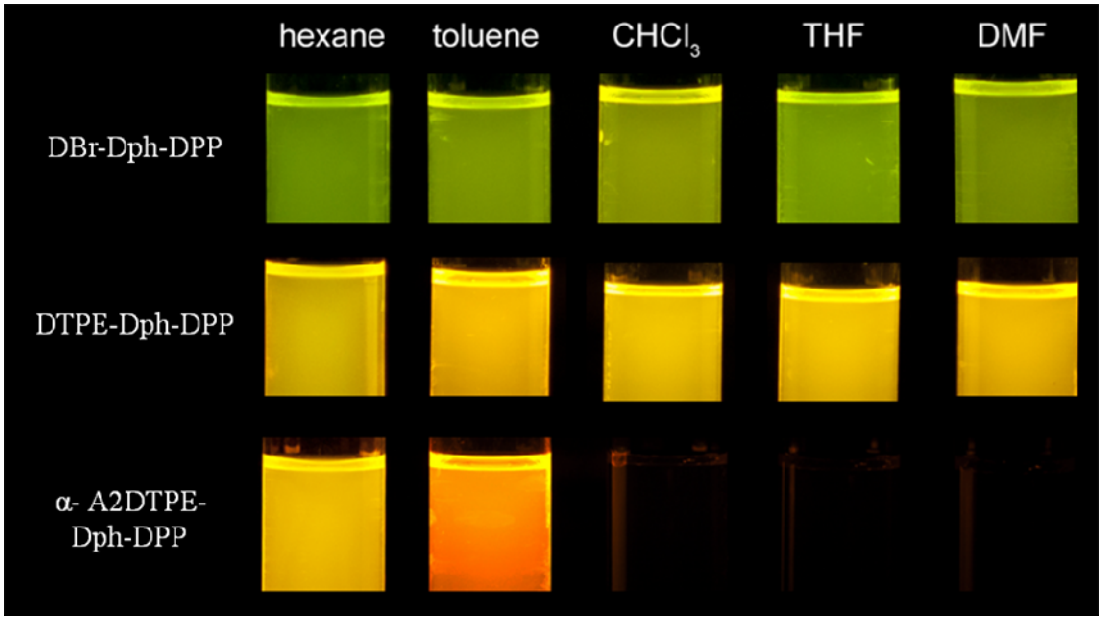


Fig. 19 Photographs of DPPs taken under UV illumination in different solvents, from left to right are: hexane, toluene, chloroform, THF, and DMF. The solutions were excited at 365 nm, concentration: 10 μM.

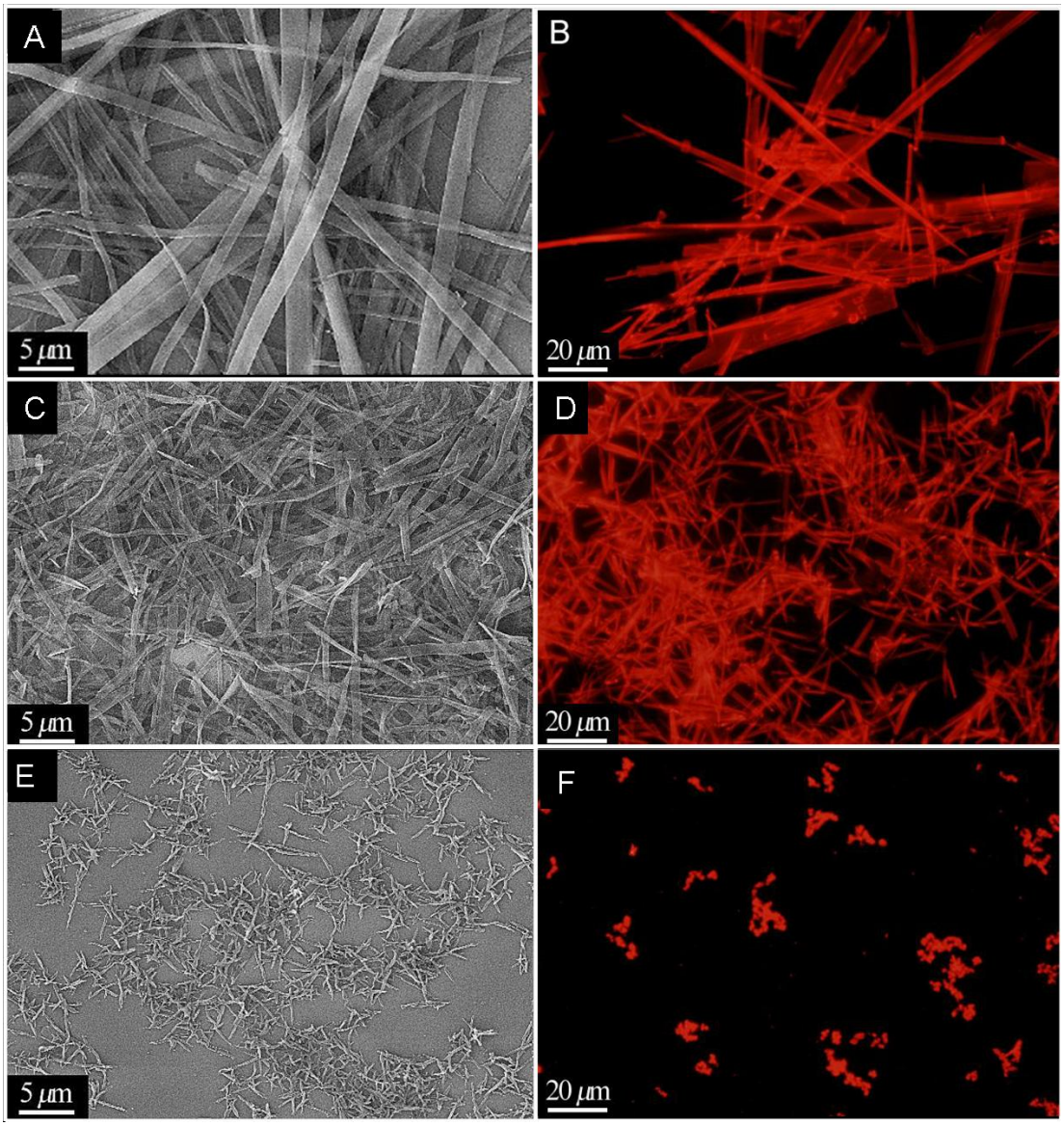


Fig. S20 Scanning electronic microscope images of α-A2DTPE-Dph-DPP (**3**) microstructures formed in THF/water mixtures with different water fractions (A: f_w = 50%; C: f_w = 60%; E: f_w = 70%) and confocal fluorescent microscopic images of **3** microstructures formed in THF/water mixtures with different water fractions (B: f_w = 50%; D: f_w = 60%; F: f_w = 70%).

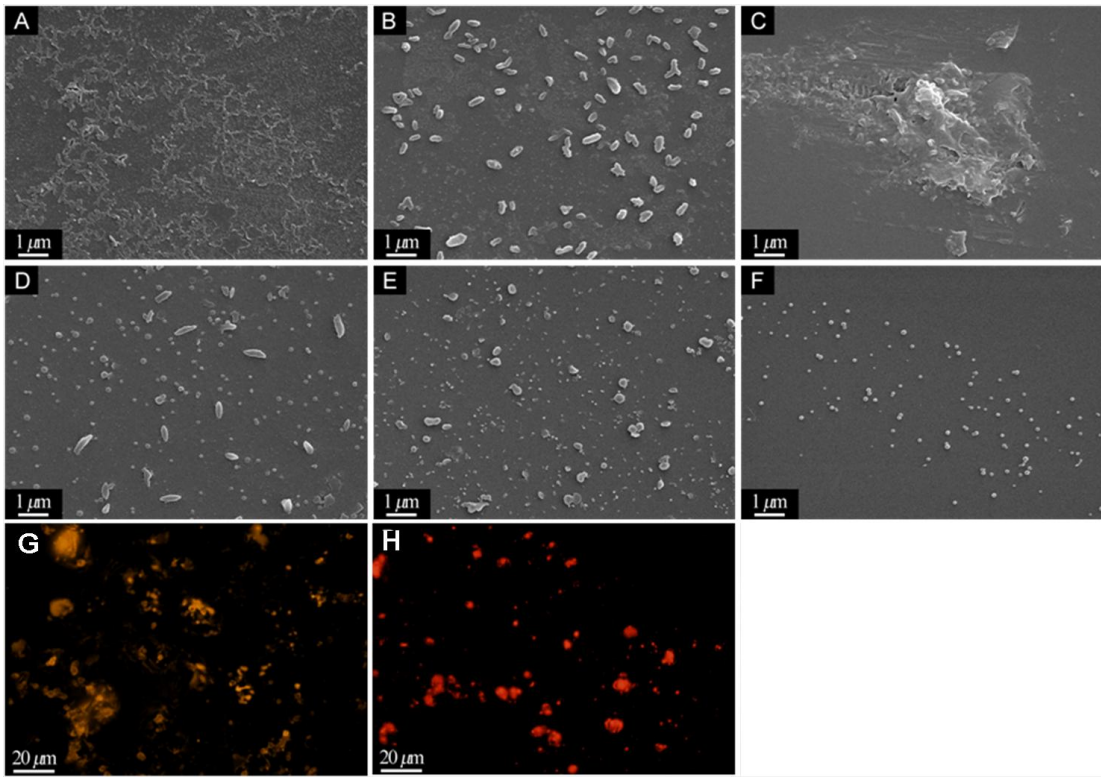


Fig. S21 (Up and middle) SEM images of the microstructures of DBr-Dph-DPP (A, B, C) and DTPE-Dph-DPP (**2**) (D, E, F) formed in THF/water mixtures with different water fractions. A, D) f_w = 50%; B, E) f_w = 60%; C, F) f_w = 70%. (**Bottom)** Fluorescence microscopic images of the microstructures of DBr-Dph-DPP (G) and DTPE-Dph-DPP (**2**) (H) formed in THF/water mixture with f_w = 50%.

Table 1 Optical and Electromnic Properties of DTPE-DPP(**1**)

solvent	Δf	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	Φ_F (%)	HOMO (eV)	LUMO (eV)	E_g (eV)
hexane	~0	498	567	2443.6	11.1			
toluene	0.014	502	576	2559.2	14.0			
chloroform	0.149	500	572	2517.5	17.4			
THF	0.210	499	572	2588.1	13.6			
DMF	0.275	494	572	2760.4	8.7			
Solid film	NA	/	595	/	11.8			
THF/H_2O(%) $0<f_w<60$	NA	/	572	/				
THF/H_2O(%) $f_w>80$	NA	/	585	/				
						-5.37	-3.18	2.19

[a] Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield (%) in dilute THF solution (soln) estimated by Rhodamine B (70% in ethanol), thin film (film) determined by a calibrated integrating sphere, E_g = energy gap calculated from the onset absorption wavelength, HOMO = the highest occupied molecular orbital determined by cyclic voltammetry, LUMO = the lowest unoccupied molecular orbital deduced from E_g and HOMO and N.D. = not detectable (signal is too weak to be accurately determined). NA = No answer.

Table S2 Optical and Electromnic Properties of DBr-Dph-DPP[a]

solvent	Δf	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	Φ_F (%)	HOMO (eV)	LUMO (eV)	E_g (eV)
hexane	~0	483	539	2151.1	100			
toluene	0.014	484	547	2379.6	90.1			
chloroform	0.149	480	541	2349.0	95.8			
THF	0.210	480	543	2417.1	95.2			
DMF	0.275	476	544	2626.1	94.7			
Solid film	NA	/	558	/	18.3			
THF/H_2O(%) $60<f_w<80$	NA	/	540	/	< 1.0			
THF/H_2O(%) $f_w>80$	NA	/	590	/	N.D.			
						-5.51	-3.17	2.34

[a] Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield (%) in dilute THF solution (soln) estimated by Rhodamine B (70% in ethanol), thin film (film) determined by a calibrated integrating sphere, E_g = energy gap calculated from the onset absorption wavelength, HOMO = the highest occupied molecular orbital determined by cyclic voltammetry, LUMO = the lowest unoccupied molecular orbital deduced from E_g and HOMO and N.D. = not detectable (signal is too weak to be accurately determined). NA = No answer.

Table S3 Optical and Electromnic Properties of DTPE-Dph-DPP(**2**)[a]

solvent	Δf	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	Φ_F (%)	HOMO (eV)	LUMO (eV)	E_g (eV)
hexane	~0	496	564	2430.8	57.6			
toluene	0.014	499	571	2526.9	58.9			
chloroform	0.149	496	566	2493.4	67.2			
THF	0.210	496	568	2555.6	43.8			
DMF	0.275	497	569	2546.0	61.8			
Solid film	NA	/	594	/	30.2			
THF/H_2O f_w= 50%	NA	/	568	/	36.5			
THF/H_2O f_w=60%	NA	/	568	/	2.2			
THF/H_2O f_w=95%	NA	/	594	/	4.1			
						-5.19	-3.17	2.22

[a] Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield (%) in dilute THF solution (soln) estimated by Rhodamine B (70% in ethanol), thin film (film) determined by a calibrated integrating sphere, E_g = energy gap calculated from the onset absorption wavelength, HOMO = the highest occupied molecular orbital determined by cyclic voltammetry, LUMO = the lowest unoccupied molecular orbital deduced from E_g and HOMO and N.D. = not detectable (signal is too weak to be accurately determined). NA = No answer.

Table S4 Optical and Electromnic Properties of α-A_2DTPE-Dph-DPP(**3**)[a]

solvent	Δf	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	Φ_F (%)	HOMO (eV)	LUMO (eV)	E_g (eV)
hexane	~0	498	564	2349.8	59.6			
toluene	0.014	501	572	2477.6	41.5			
chloroform	0.149	498	n.d.	N/A	0			
THF	0.210	500	564	2269.5	0.2			
DMF	0.275	497	N.D.	N/A	0			
Solid film	NA	/	602	/	8.6			
THF/H_2O f_w < 50%	NA	/	564 ~557	/	N.D.			
THF/H_2O f_w > 50%	NA	/	575 ~588	/	0.34			
						-5.00	-2.80	2.20

[a] Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield (%) in dilute THF solution (soln) estimated by Rhodamine B (70% in ethanol), thin film (film) determined by a calibrated integrating sphere, E_g = energy gap calculated from the onset absorption wavelength, HOMO = the highest occupied molecular orbital determined by cyclic voltammetry, LUMO = the lowest unoccupied molecular orbital deduced from E_g and HOMO and N.D. = not detectable (signal is too weak to be accurately determined). NA = No answer.

Table S5 Data Summary of the Optical and Electromnic Properties of DBr-Dph-DPP and Molecules **1**, **2**, **3**, and **4**[a]

	DBr-Dph-DPP	**1**	**2**	3	4
$\lambda_{abs,sol}$ / nm	480	499	496	500	499
$\lambda_{em,sol}$ / nm	543	572	568	564	565
$\lambda_{em,agg}$ / nm	584	585	592	588	594
$\lambda_{em,film}$ / nm	558	595	594	602	610
$\Phi_{F,sol}$ / %	95.2	13.6	43.8	0.20	0.26
$\Phi_{F,agg}$ / %	0.95	1.27	4.14	0.34	0.51
$\Phi_{F,solid}$ / %	18.3	11.8	30.2	8.6	N.D.
$HOMO_{cal}$ / eV	-5.33	-4.90	-4.98	-4.75	-4.72
$LUMO_{cal}$ / eV	-2.55	-2.28	-2.30	-2.23	-2.20
ΔE_{cal} / eV	2.78	2.62	2.68	2.52	2.48
$HOMO_{meas}$ / eV	-5.51	-5.37	-5.39	-5.00	N.D.
$LUMO_{meas}$ / eV	-3.17	-3.18	-3.17	-2.80	N.D.
ΔE_{meas} / eV	2.34	2.19	2.22	2.20	N.D.

[a] The data for are DBr-Dph-DPP and molecules **1**, **2**, **3** are extracted from Tables S1-S4; for molecule **4**, the data are obtained by measurements using the same methods as molecule **3**.

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