

Electronic Supporting Information

Tetraphenylpyrazine-based luminogens with full-colour emission

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Experimental Section

Materials: All commercially available chemicals were purchased from Energy, TCI, J&K chemistry or Beijing HWRK Chem Co., Ltd., Soochiral Chemical Reagent Co., Ltd. and used directly without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under dry nitrogen immediately before use.

Instrumentation: All ^1H and ^{13}C NMR spectra were recorded with a Bruker AV 500 spectrometer in deuterated CDCl_3 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) were tested using a GCT premier CAB048 mass spectrometer operated in MALDI-TOF mode. UV-visible absorption spectra were measured with a SHIMADZU UV-2600 spectrophotometer. PL spectra were recorded on a HORIBA Flioromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaaurus-QY. Thermogravimetric analysis (TGA) analysis was carried out on a TA TGA Q5000 absolute at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ under dry nitrogen.

Synthesis of compound 1: TPP-Br was prepared according to the literatures.¹⁻³ TPP-Br (9.24 g, 20 mmol), Bis(pinacolato)diboron (10.16 g, 40 mmol), 1,1'-Bis(diphenylphosphino)ferrocene palladium(II)dichloride $\text{Pd}(\text{dppf})\text{Cl}_2$ (730 mg, 1 mmol), and KOAc (7.85 g, 80 mmol) were added into a 500 mL two neck flask under nitrogen. Then 150 mL 1,4-dioxane was injected into the flask and the reaction was stirred and refluxed 10 h. After removing the solvent under vacuum, the mixture was dissolved in DCM and washed with water three times. The organic phase was dried over Mg_2SO_4 and concentrated. Finally the crude product was purified by a silica-gel column with DCM/hexane (1:10 by volume) as eluent. Oily product was obtained and after creation of vacuum, white solid **1** was obtained in 89.7% yield. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.76-7.75(m, 2H), 7.65-7.62 (m, 8H), 7.36-7.29 (m, 9H), 1.35 (s, 12H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 148.53, 148.47, 148.39, 148.24, 141.17, 138.43, 138.42, 138.35, 134.56, 129.88, 129.15, 128.61, 128.29, 128.23, 128.22, 83.89, 24.89.

Synthesis of DTPP: TPP-Br (460 mg, 1.0 mmol), **1** (510 mg, 1.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.05 mmol) and K_2CO_3 (280 mg, 2.0 mmol) were added into a 250 mL two neck flask under nitrogen. Then 35 mL THF and 15mL H_2O were injected and the mixture was refluxed overnight. When the mixture was cooled into the room temperature, a mass of white precipitation can be found in the flask. After filtrating and was washed with ethyl acetate, the crude product was obtained in 78.3% yield. Finally, the crude product was treated with sublimation.

^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.74-7.73 (m, 4H), 7.71-7.69 (m, 4H), 7.67-7.64 (m, 8H), 7.60-7.58 (m, 4H), 7.38-7.31 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 148.43, 148.38, 147.82, 140.52, 138.51, 138.45, 138.43, 137.64, 130.35, 129.89, 128.69, 128.64, 128.34, 128.25, 128.24, 126.81. HRMS (MALDI TOF): m/z 766.3129 [M^+], calcd for $\text{C}_{56}\text{H}_{38}\text{N}_4$ 766.3096.

Synthesis of DTPP-Ph: The reaction and purification methods were similar to that of DTPP. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.77-7.74 (m, 4H), 7.73-7.70 (m, 8H), 7.68-7.65 (m, 8H), 7.64-7.61 (m, 4H), 7.38-7.31 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 148.43, 148.37, 147.86, 140.63, 139.59, 138.52, 138.47, 138.44, 137.50, 130.37, 129.90, 128.69, 128.64, 128.35, 128.26, 128.24, 127.46, 127.42, 127.39, 126.76. HRMS (MALDI TOF): m/z 842.3433 [M^+], calcd for $\text{C}_{62}\text{H}_{42}\text{N}_4$ 842.3409.

Synthesis of (DTPP-BT): The reaction and purification methods were similar to that of DTPP. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 8.00-7.98 (m, 4H), 7.87-7.83 (m, 6H), 7.78-7.74 (m, 4H), 7.71-7.65 (m, 8H), 7.40-7.32 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 154.04, 148.39, 147.68, 138.49, 138.46, 138.44, 138.42, 137.51, 132.82, 130.15, 129.95, 129.91, 129.06, 128.76, 128.67, 128.40, 128.26, 128.15. HRMS (MALDI TOF): m/z 900.3055 [M^+], calcd for $\text{C}_{62}\text{H}_{40}\text{N}_6\text{S}$ 900.3035.

Synthesis of DTPP-T: The reaction method was similar to that of DTPP, and the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow green solid was obtained in 83.1% and then treated with sublimation. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.71-7.68 (m, 8H), 7.66-7.64 (m, 8H), 7.58-7.57 (m, 4H), 7.37-7.30 (m, 20H). ^{13}C NMR (126 MHz, CDCl_3), δ (TMS, ppm): 148.36, 148.33, 148.26, 147.53, 143.41, 138.45, 138.40, 138.38, 137.53, 134.34, 130.45, 129.88, 129.86, 128.74, 128.66, 128.65, 128.39, 128.25, 128.24, 125.28, 124.52. HRMS (MALDI TOF): m/z 848.2972 [M^+], calcd for $\text{C}_{60}\text{H}_{40}\text{N}_4\text{S}$ 848.2974.

Synthesis of DTPP-TO: The reaction method was similar to that of DTPP, and the crude product was purified by a silica-gel column with DCM/hexane (1:4 by volume) as eluent. Yellow solid was obtained in 79.6% and then treated with sublimation. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.79-7.77 (m, 4H), 7.76-7.73 (m, 4H), 7.69-7.64 (m, 12H), 7.41-7.31 (m, 18H), 7.05 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 148.71, 148.47, 148.45, 146.86, 141.45, 140.39, 138.24, 138.23, 138.13, 130.73, 129.90, 129.88, 129.86, 128.96, 128.78, 128.76, 128.52, 128.30, 128.27, 127.13, 126.15, 120.79. HRMS (MALDI TOF): m/z 880.2852 [M^+], calcd for $\text{C}_{60}\text{H}_{40}\text{N}_4\text{O}_2\text{S}$ 880.2872.

Synthesis of DTPP-TBTT: The reaction and purification methods were similar to that of DTPP. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 8.14-8.13 (d, 2H), 7.92 (s, 2H), 7.73-7.70 (m, 8H), 7.69-7.65 (m, 12H), 7.47-7.46 (d, 2H), 7.39-7.31 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (TMS, ppm): 152.56, 148.40, 148.38, 148.32, 147.53, 145.05, 139.02, 138.46, 138.42, 138.39, 137.79, 134.24, 130.49, 129.88, 128.76, 128.69, 128.67, 128.40, 128.27, 128.24, 125.78, 125.49, 125.40, 124.50. HRMS (MALDI TOF): m/z 1064.2794 [M^+], calcd for $\text{C}_{70}\text{H}_{44}\text{N}_6\text{S}_3$ 1064.2790.

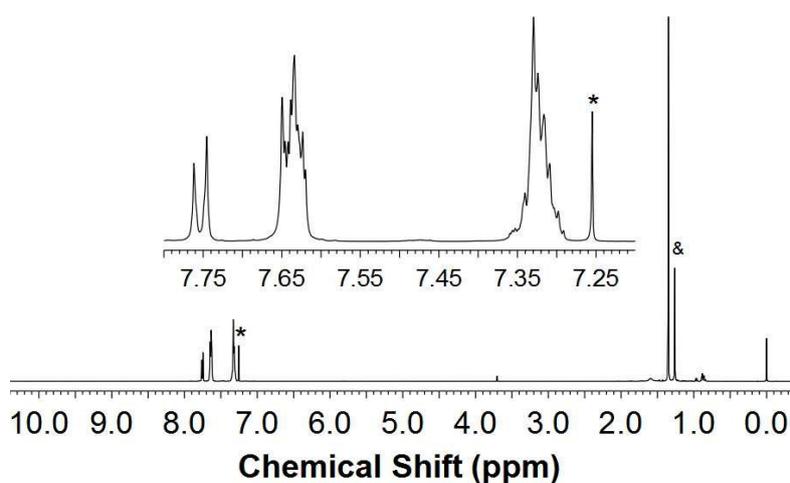


Fig. S1. ^1H NMR spectrum of **1** in CDCl_3 . The solvent peak is marked with asterisk and the & refers to the H of the unreacted bis(pinacolato)diboron.

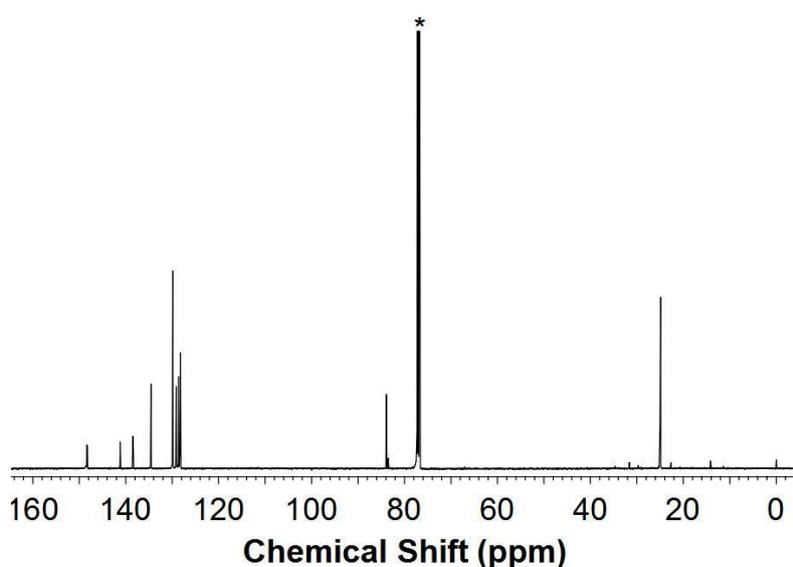


Fig. S2. ^{13}C NMR spectrum of **1** in CDCl_3 . The solvent peak is marked with asterisk.

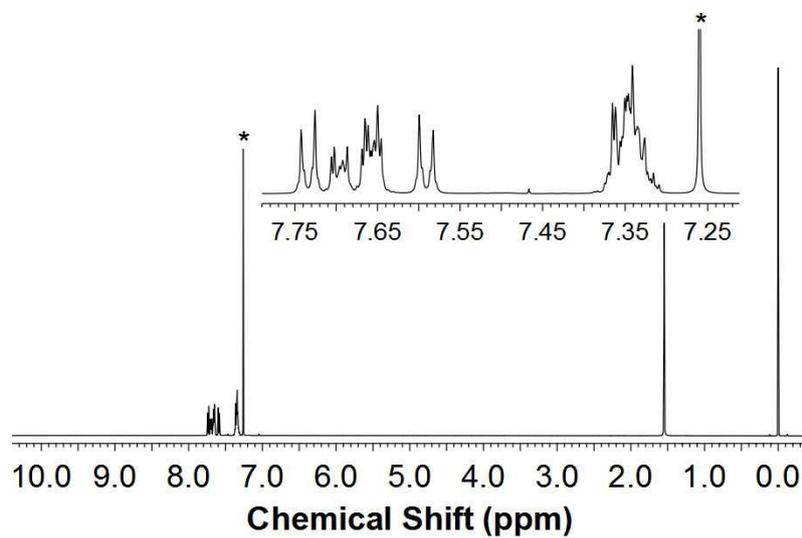


Fig. S3. ¹H NMR spectrum of DTPP in CDCl₃. The solvent peak is marked with asterisk.

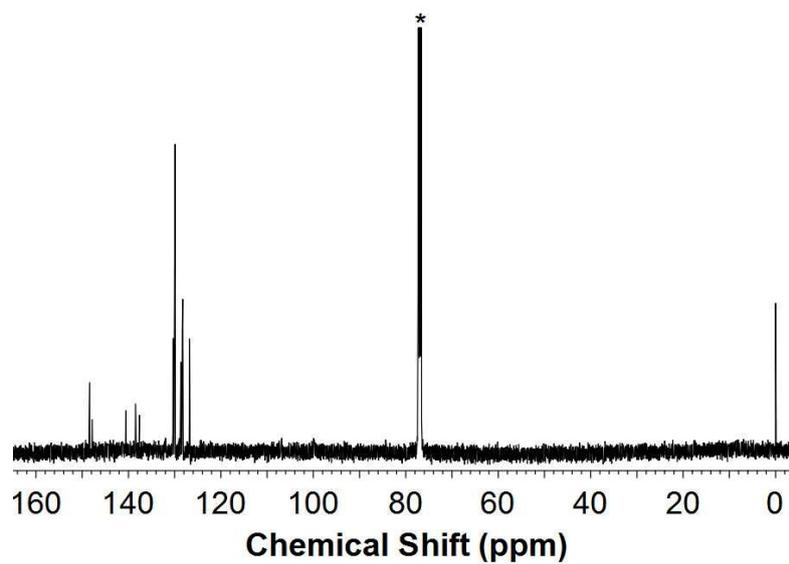


Fig. S4. ¹³C NMR spectrum of DTPP in CDCl₃. The solvent peak is marked with asterisk.

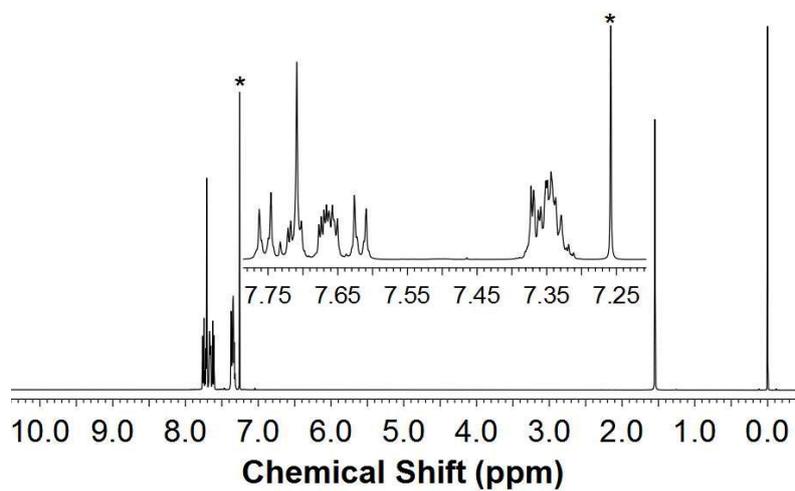


Fig. S5. ^1H NMR spectrum of DTPP-Ph in CDCl_3 . The solvent peak is marked with asterisk.

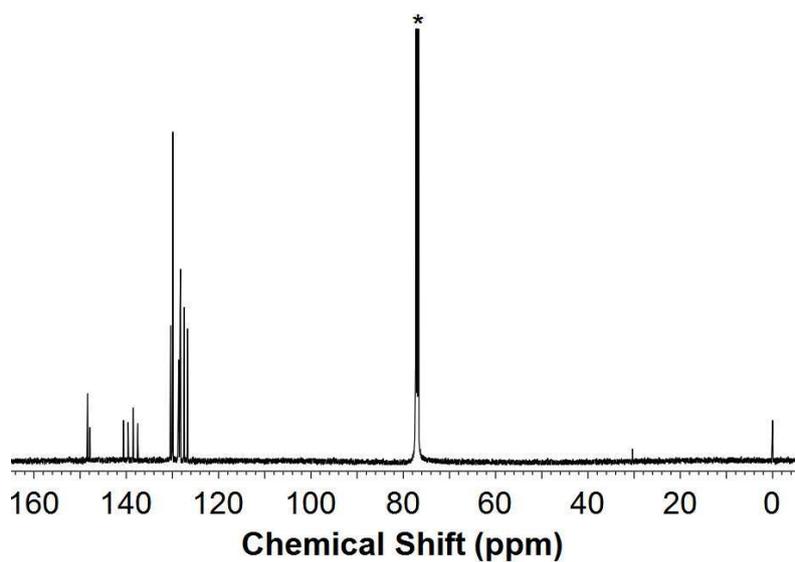


Fig. S6. ^{13}C NMR spectrum of DTPP-Ph in CDCl_3 . The solvent peak is marked with asterisk.

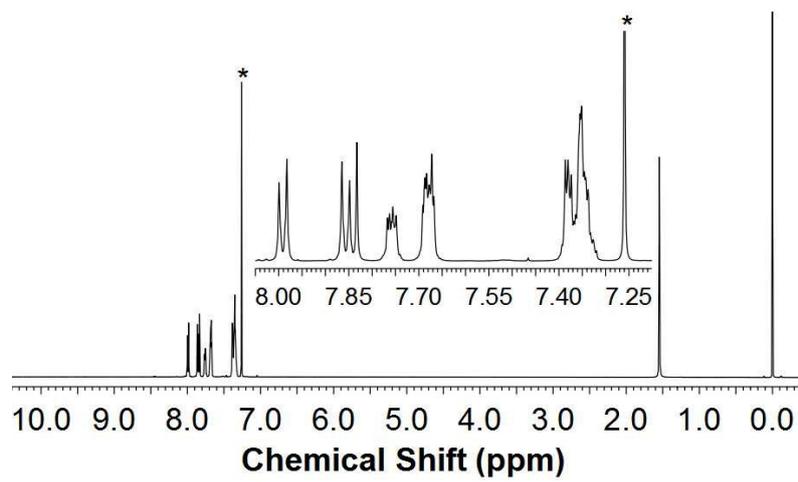


Fig. S7. ^1H NMR spectrum of DTPP-BT in CDCl_3 . The solvent peak is marked with asterisk.

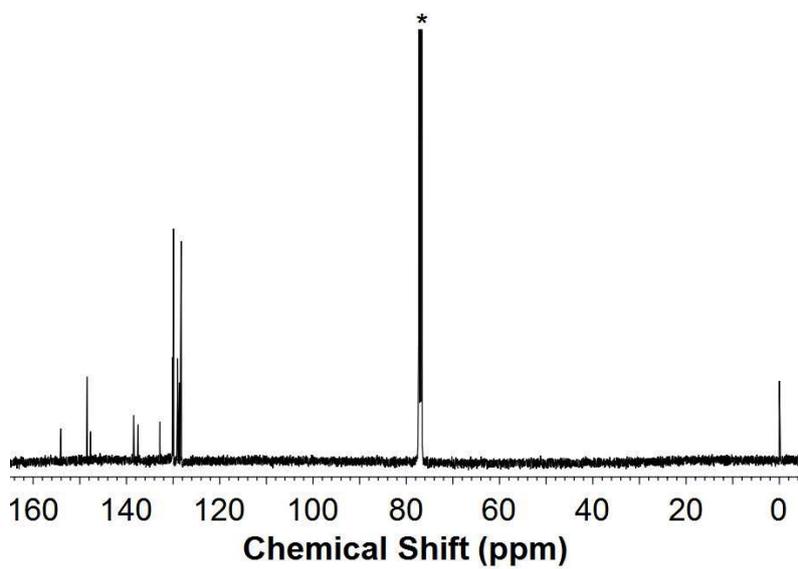


Fig. S8. ^{13}C NMR spectrum of DTPP-BT in CDCl_3 . The solvent peak is marked with asterisk.

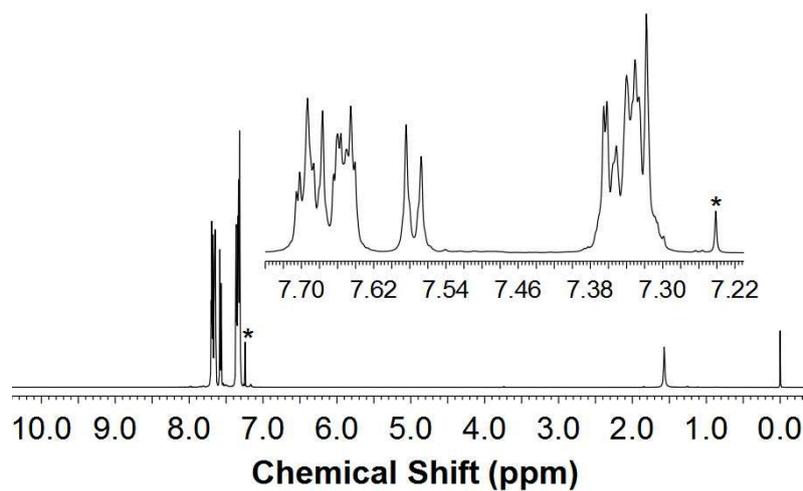


Fig. S9. ^1H NMR spectrum of DTPP-T in CDCl_3 . The solvent peak is marked with asterisk.

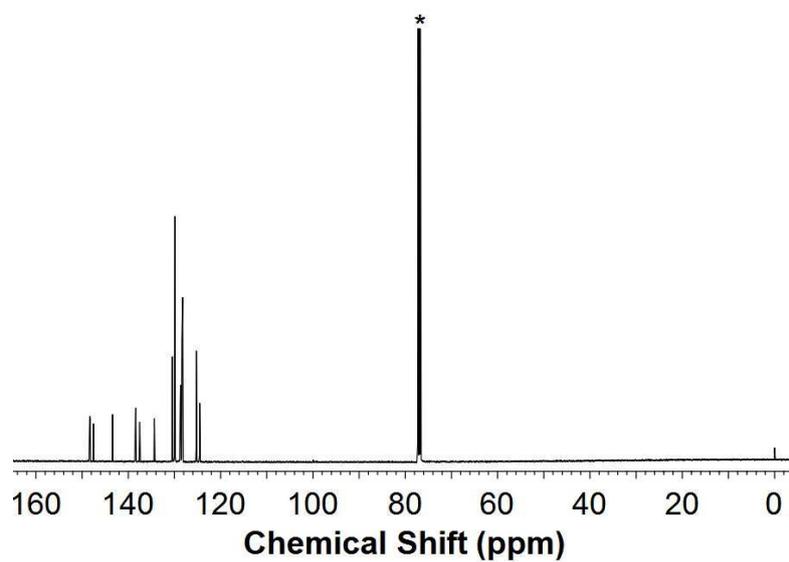


Fig. S10. ^{13}C NMR spectrum of DTPP-T in CDCl_3 . The solvent peak is marked with asterisk.

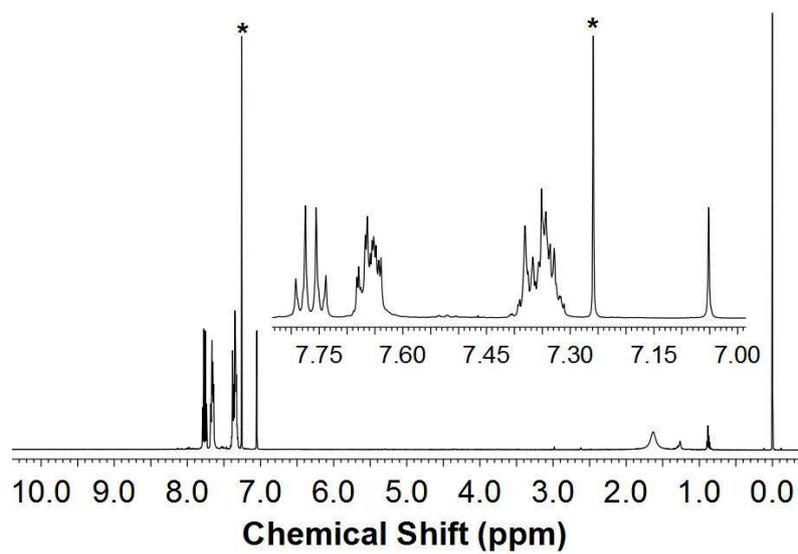


Fig. S11. ^1H NMR spectrum of DTPP-TO in CDCl_3 . The solvent peak is marked with asterisk.

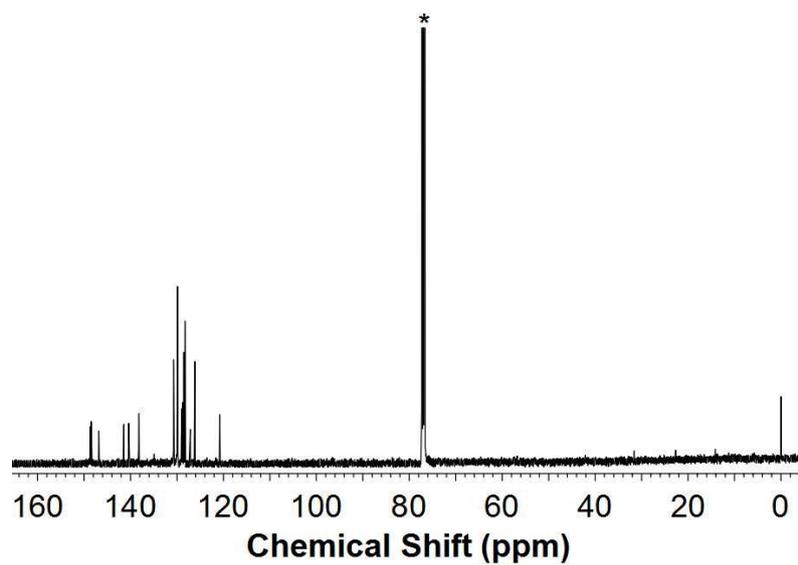


Fig. S12. ^{13}C NMR spectrum of DTPP-TO in CDCl_3 . The solvent peak is marked with asterisk.

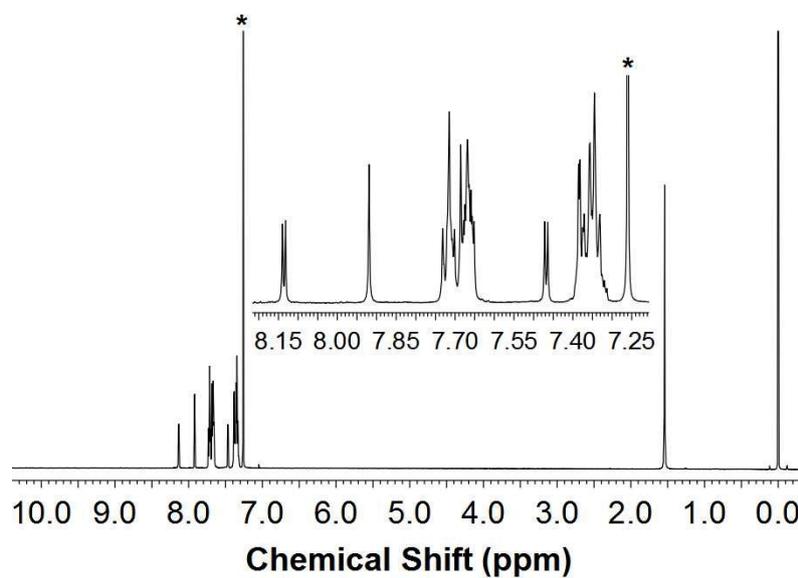


Fig. S13. ^1H NMR spectrum of DTPP-TBTT in CDCl_3 . The solvent peak is marked with asterisk.

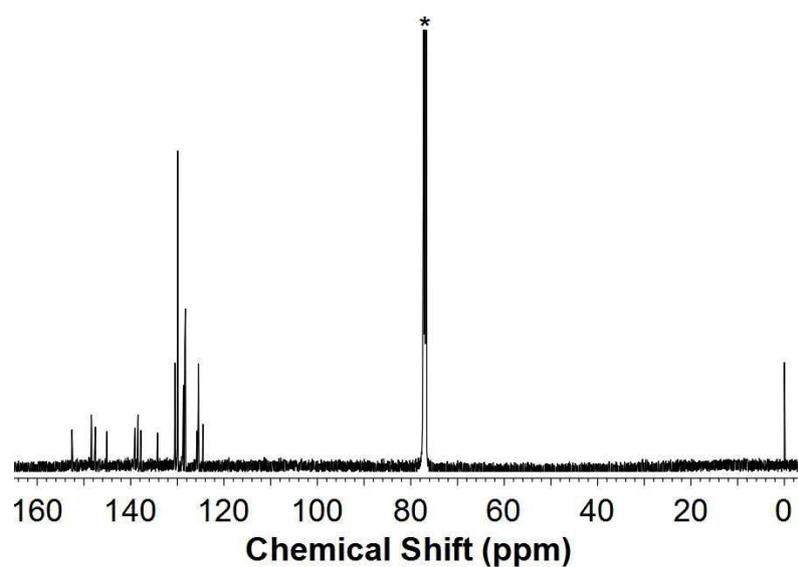


Fig. S14. ^{13}C NMR spectrum of DTPP-TBTT in CDCl_3 . The solvent peak is marked with asterisk.

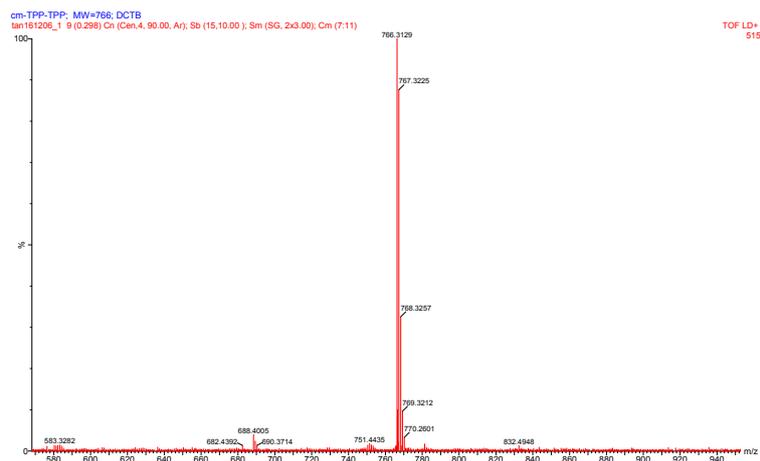


Fig. S15. HRMS spectra of DTPP.

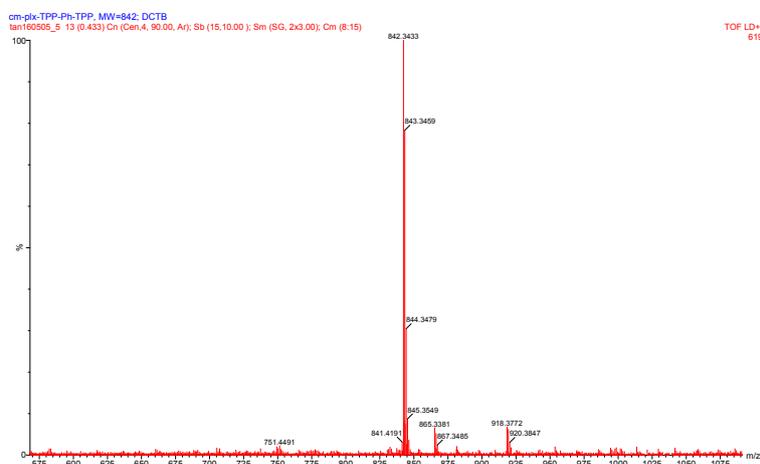


Fig. S16. HRMS spectra of DTPP-Ph.

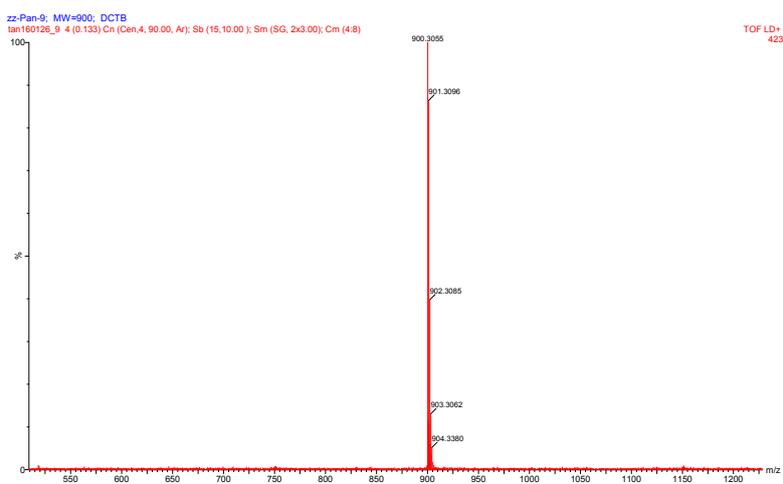


Fig. S17 HRMS spectra of DTPP-BT

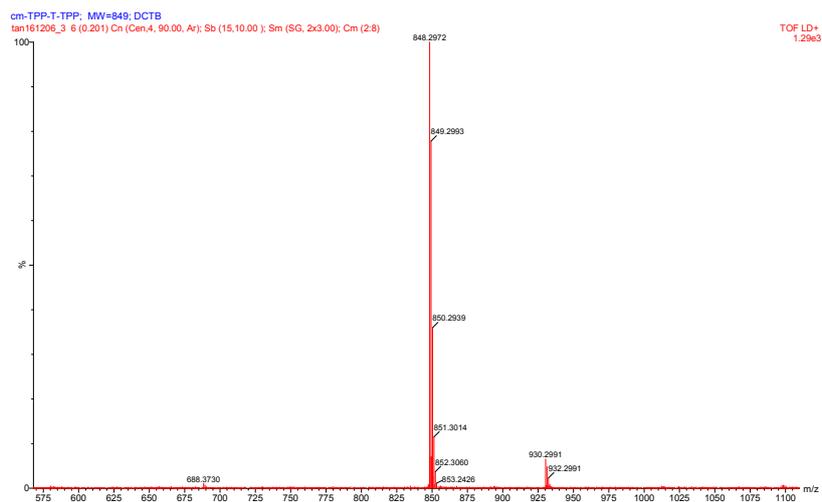


Fig. S18. HRMS spectra of DTPP-T.

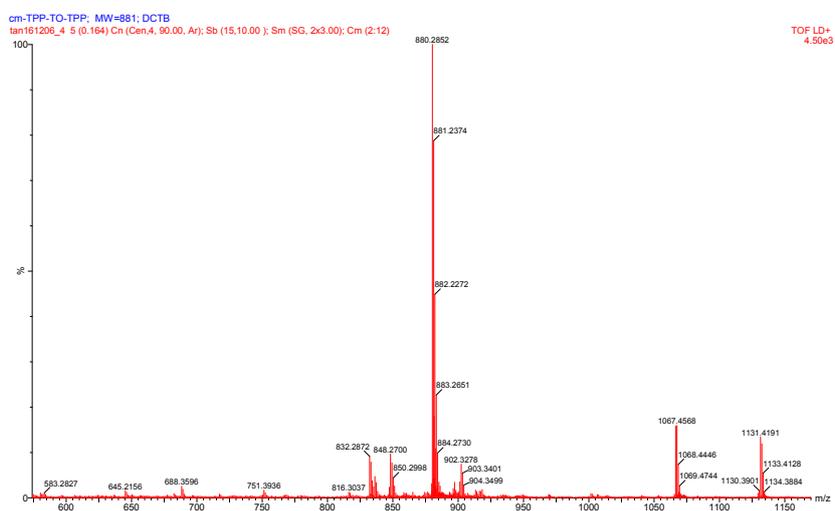


Fig. S19. HRMS spectra of DTPP-TO.

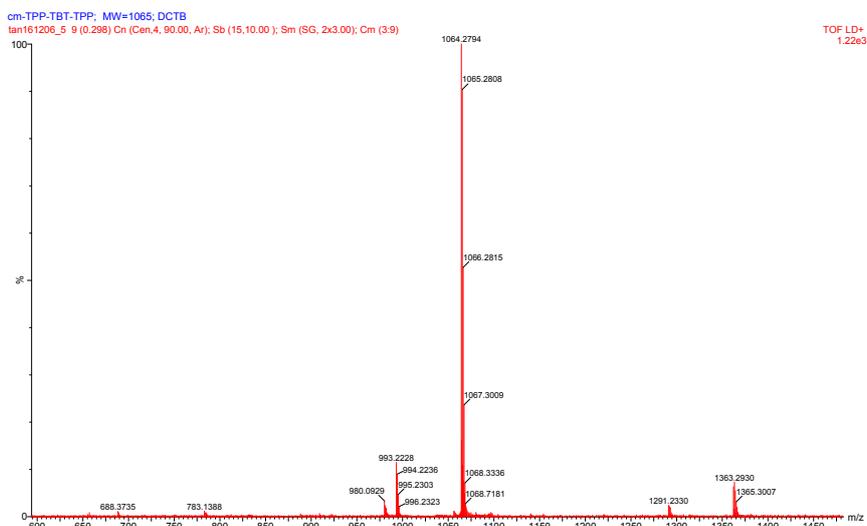


Fig. S20. HRMS spectra of DTPP-TBTT.

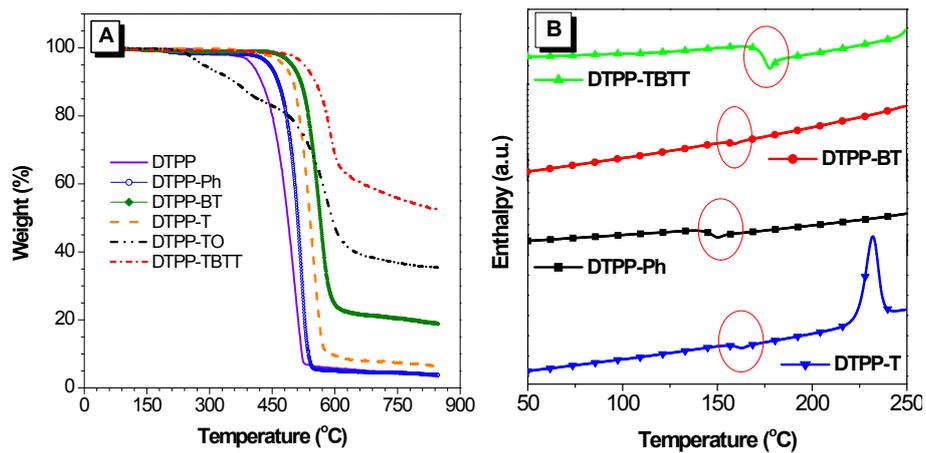


Fig. S21. TGA and DSC curves of DTTP, DTTP-Ph, DTTP-BT, DTTP-T, DTTP-TO and DTTP-TBTT.

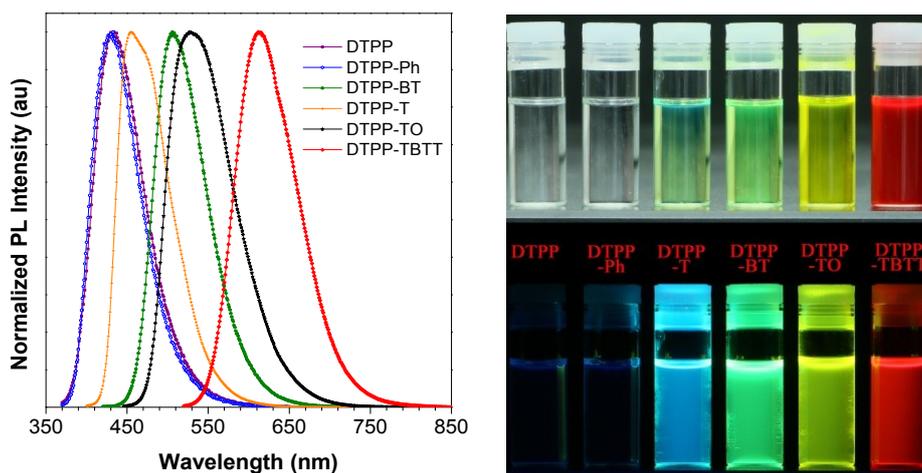


Fig. S22. A) PL spectra of DTTP, DTTP-Ph, DTTP-BT, DTTP-T, DTTP-TO and DTTP-TBTT in THF solutions, concentration: 10 μ M, B) Photos of these TPP derivatives in THF solutions, taken under daylight and irradiation of a UV lamp (365 nm).

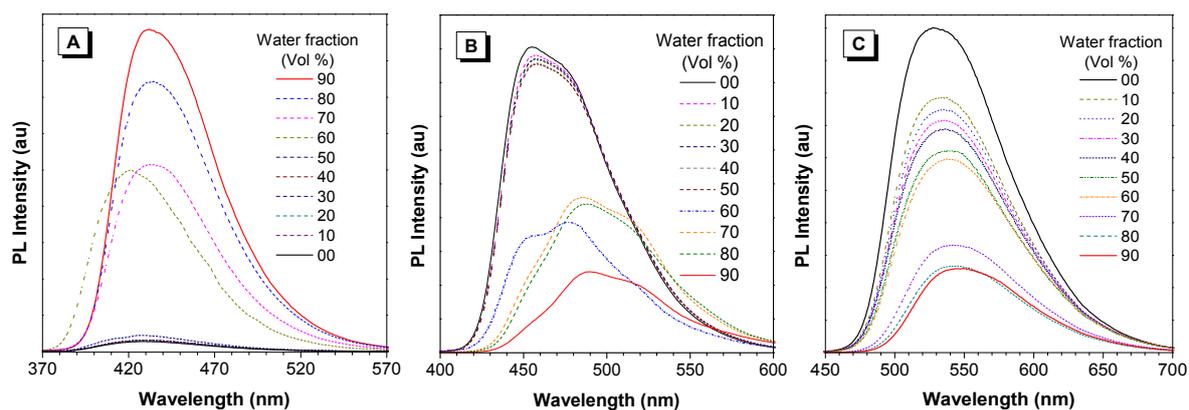


Fig. S23. PL spectra of A) DTPP-Ph, B) DTPP-T, and C) DTPP-TO in THF/H₂O mixtures with different water fractions. Concentration: 10 μ M

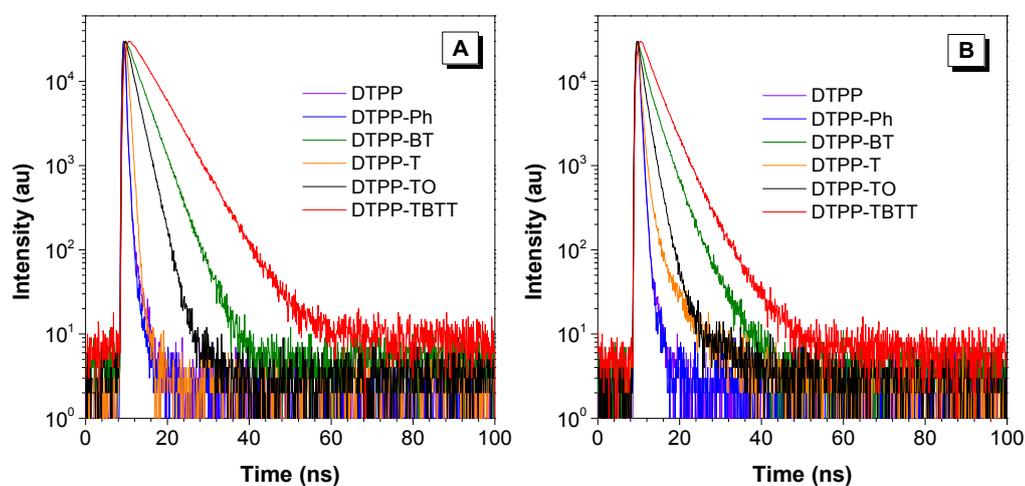


Fig. S24 The time-resolved fluorescence spectra of these TPP derivatives A) in THF solution, concentration: 10 μ M; B) in solid films.

Table S1 The theoretical and experimental energy levels of DTPP, DTPP-Ph, DTPP-BT, DTPP-T, DTPP-TO and DTPP-TBTT.

Compound	Theoretical energy level ^a [eV]			Experimental energy level ^b [eV]		
	HOMO	LUMO	E_g	HOMO ^c	LUMO ^d	E_g^e
DTPP	-5.44	-1.79	3.65	-5.74	-2.61	3.13
DTPP-Ph	-5.44	-1.76	3.68	-5.81	-2.68	3.13
DTPP-BT	-5.44	-2.47	2.97	-5.78	-3.08	2.70
DTPP-T	-5.23	-1.92	3.31	-5.55	-2.73	2.82
DTPP-TO	-5.50	-2.61	2.89	-5.85	-3.35	2.50
DTPP-TBTT	-5.03	-2.70	2.33	-5.33	-3.26	2.07

^a. calculated by DFT/B3LYP/6-31G(d). ^b. Determined by cyclic voltammetry. ^c. $E_{\text{HOMO}} = -(E_{\text{onset}} + 4.4)$ eV. ^d.

$E_{\text{HOMO}} = E_{\text{LUMO}} + E_g$. ^e. $E_g = 1240/\lambda_{\text{edge}}$.

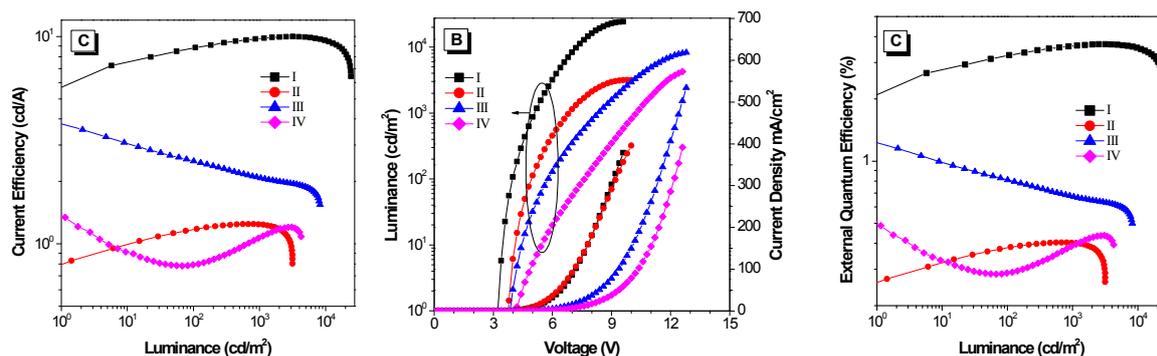


Fig. S25. A) current density-voltage-luminance characteristics, B) dependence of current efficiency, C) external quantum efficiency of the devices I-IV.

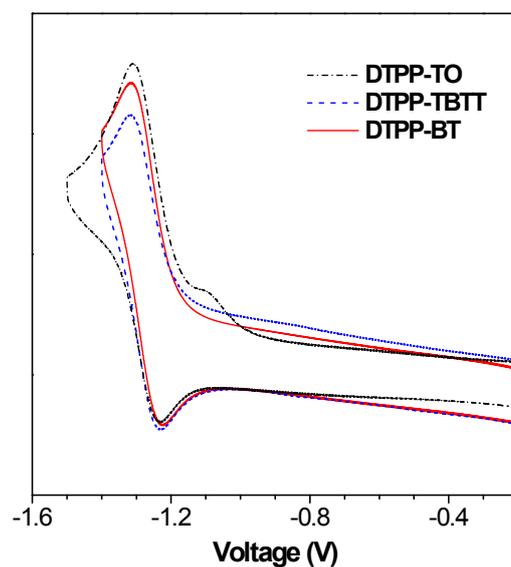


Fig. S26. Cyclic voltammograms of DTPP-BT, DTPP-TO and DTPP-TBTT, measured in DMF containing 0.1 M tetra-n-butylammonium hexafluorophosphate in reduction process, scan rate: 100 mV s⁻¹.

Reference

1. L. Pan, W. Luo, M. Chen, J. Liu, L. Xu, R. Hu, Z. Zhao, A. Qin, and B. Z. Tang, *Chin. J. Org. Chem.*, 2016, **36**, 1316-1324.
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3. P. Karastatiris, J. A. Mikroyannidis, I. K. Spiliopoulos, A. P. Kulkarni and S. A. Jenekhe, *Macromolecules*, 2004, **37**, 7867-7878.