

Supporting Information

Efficient white light-emitting polymers from dual thermally activated delayed fluorescence chromophores for non-doped solution processed white electroluminescent devices

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Materials synthesis and characterizations

2-Bromo-9H-thioxanthen-9-one 10,10-dioxide (**1**) was synthesized according to the following reference.¹

2-(4-(Diphenylamino)phenyl)-9H-thioxanthen-9-one-10,10-dioxide (**2**): Compound (**4**) (0.20 g, 0.63 mmol), 4-(diphenylamino)phenylboronic acid (0.20 g, 0.69 mmol) and 2 M Na₂CO₃ (3 ml) were mixed in 2-neck round bottom flask 100 ml. THF (30 ml) was poured in the mixture followed by degassing under N₂ for 5 minutes. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.036 g, 0.031 mmol) was added following degassing under N₂ for 5 minutes. The mixture was refluxed under N₂ for 24 h. After cooling to room temperature, water (50 ml) was added to the solution and extracted by CH₂Cl₂ (50 ml x 3). The combined organic phase was washed in water (50 ml), brine solution (50 ml) and dried over with anhydrous Na₂SO₄. The solvent was evaporated until drying out. The crude product was purified by column chromatography eluting with a mixture of CH₂Cl₂ and hexane (1:1) followed by recrystallization with a mixture of CH₂Cl₂ and hexane to afford red orange solids (0.26 g, 85%). ¹H NMR (600 MHz, CDCl₃) δ = 8.51 (d, J = 1.6 Hz, 1H), 8.36 (dd, J = 7.9, 1.5 Hz, 1H), 8.20 (d, J = 8.1 Hz, 2H), 8.03 (dd, J = 8.2, 1.5 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.31 (t, J = 7.5 Hz, 4H), 7.16 (d, J = 8.0 Hz, 6H), 7.09 (t, J = 7.3 Hz, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 178.75, 149.22, 147.30, 145.94, 141.36, 138.48, 134.77, 133.28, 132.10, 131.27, 131.05, 130.02, 129.63, 129.35, 128.16, 126.80,

125.26, 124.41, 123.92, 123.65, 122.95 ppm. HRMS MADI-TOF (m/z) calcd for $C_{31}H_{21}NO_3S$: 487.1242; found 488.2588 (MH⁺).

2-(4-(Bis(4-bromophenyl)amino)phenyl)-9H-thioxanthen-9-one-10,10-dioxide (M1): Compound **(5)** (0.30 g, 0.62 mmol) was dissolved in chloroform at room temperature. Then, the mixture was moved to ice bath. *N*-Bromosuccinimide (NBS) (0.23 g, 1.30 mmol) was dissolved in CH_2Cl_2 and slowly added by dropwise at 0°C. After completed, the reaction was plugged off silica eluting with CH_2Cl_2 . The solvent was removed until dry out. The crude product was purified by recrystallization with a mixture of CH_2Cl_2 and hexane to afford yellow solids (0.21 g, 81 %). ¹H NMR (600 MHz, $CDCl_3$) δ = 8.51 (d, J = 1.8 Hz, 1H), 8.37 (dd, J = 7.9, 1.2 Hz, 1H), 8.21 (t, J = 8.3 Hz, 2H), 8.03 (dd, J = 8.2, 1.9 Hz, 1H), 7.89 (t, J = 7.6 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.6 Hz, 4H), 7.15 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.7 Hz, 4H) ppm. ¹³C NMR (150 MHz, $CDCl_3$) δ = 178.69, 148.20, 146.07, 145.63, 141.32, 138.88, 134.85, 133.34, 132.80, 132.43, 132.27, 131.31, 130.96, 129.37, 128.49, 126.97, 126.38, 124.48, 123.77, 123.69, 116.75 ppm. HRMS APCI-QTOF (m/z) calcd for $C_{31}H_{19}Br_2NO_3S$: 644.9432; found 645.8822 (MH⁺).

3,6-Di-tert-butyl-9-(4-((4-fluorophenyl)sulfonyl)phenyl)-9H-carbazole (4): A suspension of 3,6-di-*tert*-butyl-carbazole (1.12 g, 4.0 mmol) and 60% sodium hydride (0.48 g, 12.0 mmol) in dimethylformamide (100 ml) was stirred under nitrogen atmosphere at room temperature for 30 min. Under vigorous stirring, bis(4-fluorophenyl)sulfone **(3)** (4.06 g, 16.0 mmol) was added. The mixture was stirred at room temperature for 2 hours. After that the reaction was quenched with water and dichloromethane (50 ml) was added. The organic phase was washed with water (50 ml x 2) and brine solution (50 ml), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed to dryness, and the residue was purified by silica gel column chromatography (SiO_2 , CH_2Cl_2 /hexane) followed by recrystallization with a mixture of dichloromethane and methanol to afford the product as white solids (1.58 g, 77%); ¹H-NMR (600 MHz, $CDCl_3$) δ = 8.24 (d, 2H, J = 8.4 Hz) 8.13 (m, 4H), 8.06 (m, 1H), 7.81 (d, 2H, J = 8.4 Hz), 7.75 (d, 1H, J = 8.4 Hz), 7.46 (m, 3H), 7.39 (d, 1H, J = 8.6 Hz), 1.46 (s, 18H) ppm; ¹³C-NMR (150 MHz, $CDCl_3$) δ = 144.1, 138.7, 138.3, 138.2, 129.6, 129.4, 126.6, 126.5, 124.1, 123.9, 116.5, 109.2, 109.1, 34.8, 31.9 ppm. HRMS MALDI-TOF (m/z) calcd for $C_{32}H_{32}FNO_2S$: 513.2138; found 513.4738 (M⁺).

*2,7-Dibromo-9-(4-((4-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)phenyl)sulfonyl)phenyl)-9H-carbazole (M2)*: A suspension of 2,7-dibromo-9H-carbazole (0.48 g, 1.5 mmol) and 60% sodium hydride (0.12 g, 3.0 mmol) in dimethylformamide (50 ml) was heated at 70 °C under nitrogen atmosphere. At this temperature and under vigorous stirring, compound **4** (0.51 g, 1.0 mmol) was added. The mixture was stirred at 70 °C for 24 hours. After cooling to room temperature, the reaction was quenched with water and dichloromethane (50 ml) was added. The organic phase was washed with water (50 ml x 2) and brine solution (50 ml), dried

over anhydrous Na_2SO_4 and filtered. The solvent was removed to dryness, and the residue was purified by silica gel column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{hexane}$) followed by recrystallization with a mixture of dichloromethane and methanol to afford white solids (0.67 g, 94%); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ = 8.31 (d, 2H, J = 8.7 Hz), 8.26 (d, 2H, J = 8.7 Hz), 8.13 (s, 2H), 7.94 (d, 2H, J = 8.3 Hz), 7.84 (d, 2H, J = 8.5 Hz), 7.75 (d, 2H, J = 8.5 Hz), 7.55 (dd, 2H), 7.44-7.47 (m, 5H), 1.46 (s, 18H) ppm; $^{13}\text{C-NMR}$ (150 MHz, CDCl_3) δ = 144.2, 143.5, 141.3, 141.0, 140.9, 138.2, 130.0, 129.8, 127.4, 126.6, 124.6, 124.3, 124.2, 124.0, 122.3, 121.9, 121.7, 120.4, 116.5, 112.9, 112.6, 109.2, 34.8, 31.9 ppm; HRMS APCI-QTOF (m/z) calcd for $\text{C}_{44}\text{H}_{38}\text{Br}_2\text{N}_2\text{O}_2\text{S}$: 816.1021; found 817.0843 (MH⁺).

References

¹ Wang, H.; Xie, L.; Peng, Q.; Meng, L.; Wang, Y.; Yi, Y.; Wang, P., Novel thermally activated delayed fluorescence materials-thioxanthone derivatives and their applications for highly efficient OLEDs. *Adv Mater* 2014, 26 (30), 5198-204.

Additional Characterization data

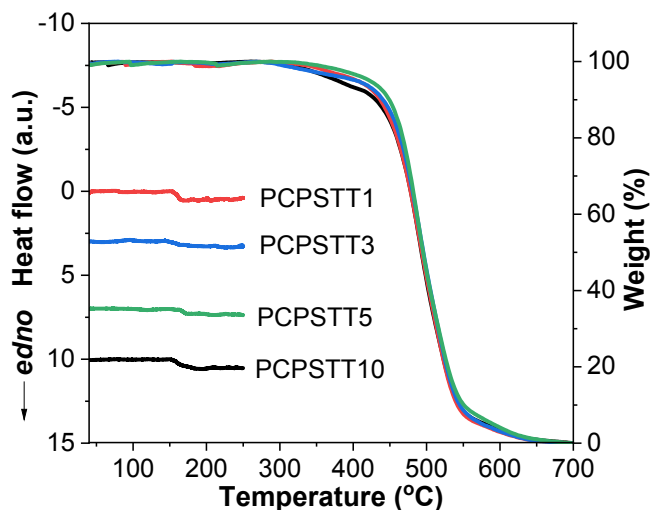


Fig. S1 TGA and DSC thermograms of PCPSTTx measured N_2 flow at heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

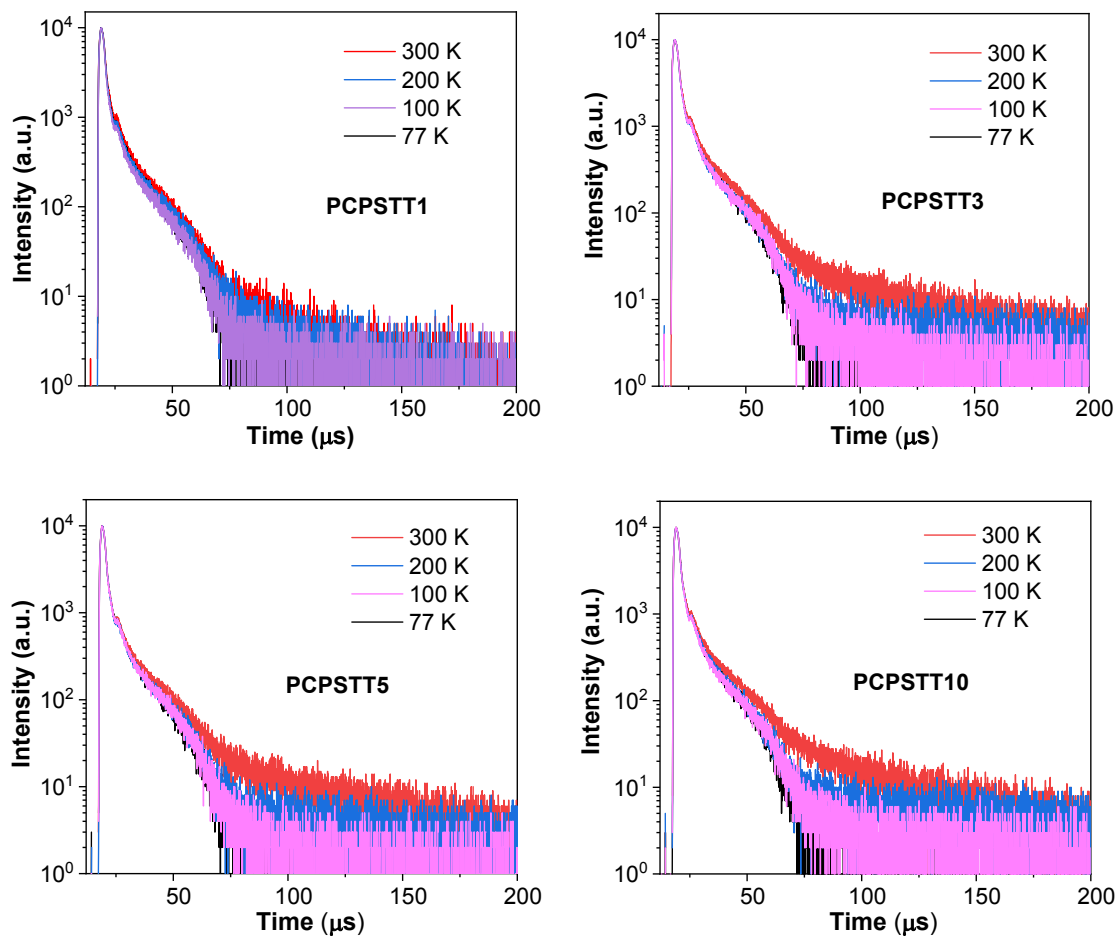


Fig. S2 The temperature-dependent transient PL decays of 1wt% doped in Zeonex films of PCPSTTx measured at 77 to 300 K.

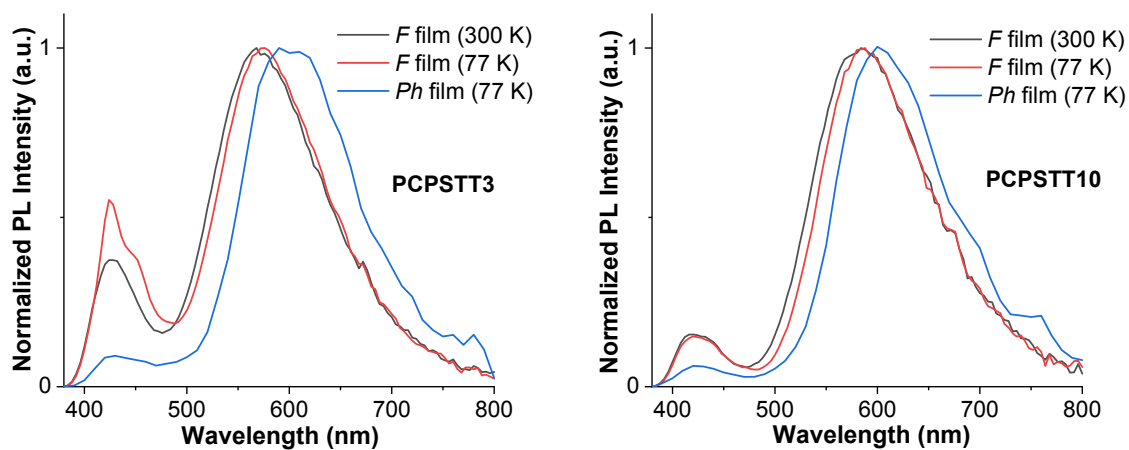


Fig. S3 The fluorescence (*F*) and phosphorescence (*Ph*) spectra of PCPSTT3 and PCPSTT10 at 1wt% doped in Zeonex films measured at 300 K and 77 K, respectively.

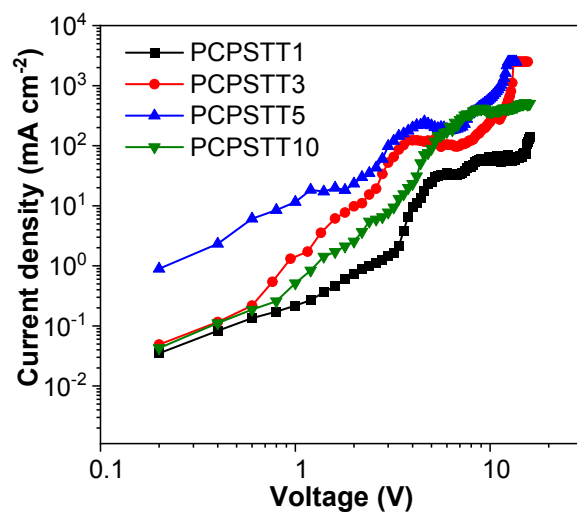


Fig. S4 Current density-voltage (J-V) plots of the electron only devices (ITO/PEDOT:PSS (35 nm)/Al (50 nm)/PCPSTTx (130 nm)/TmPyPB (10 nm)/Li (0.5 nm)/Al (80 nm)).

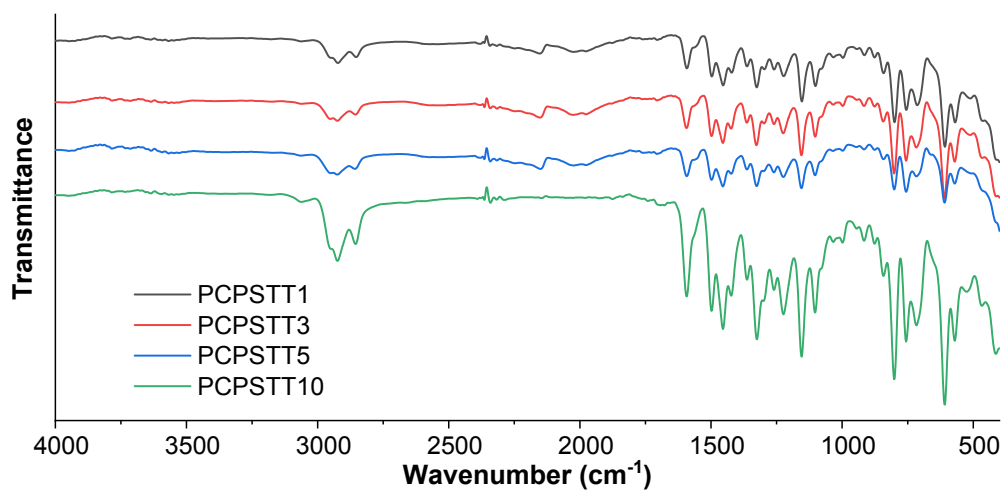
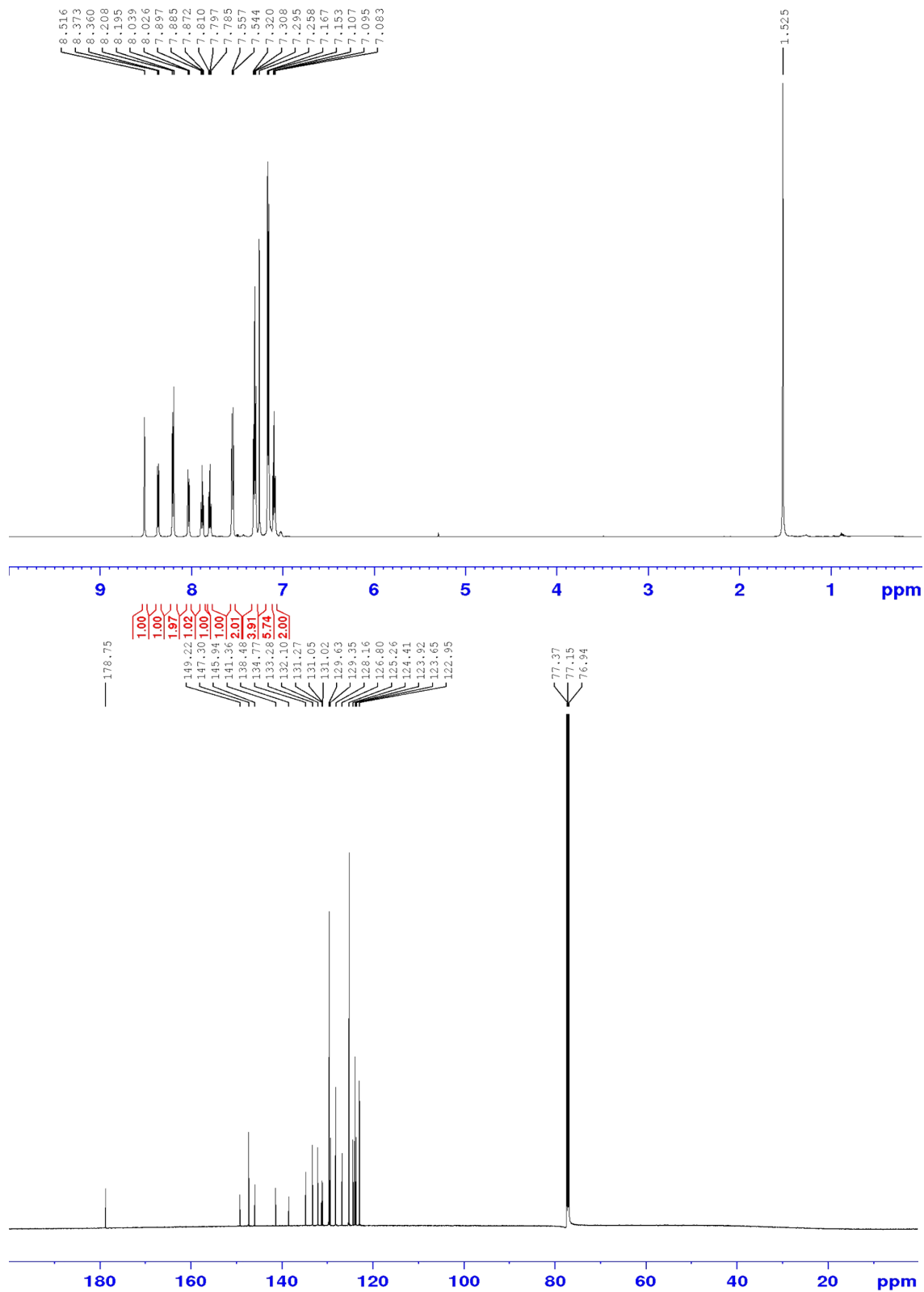


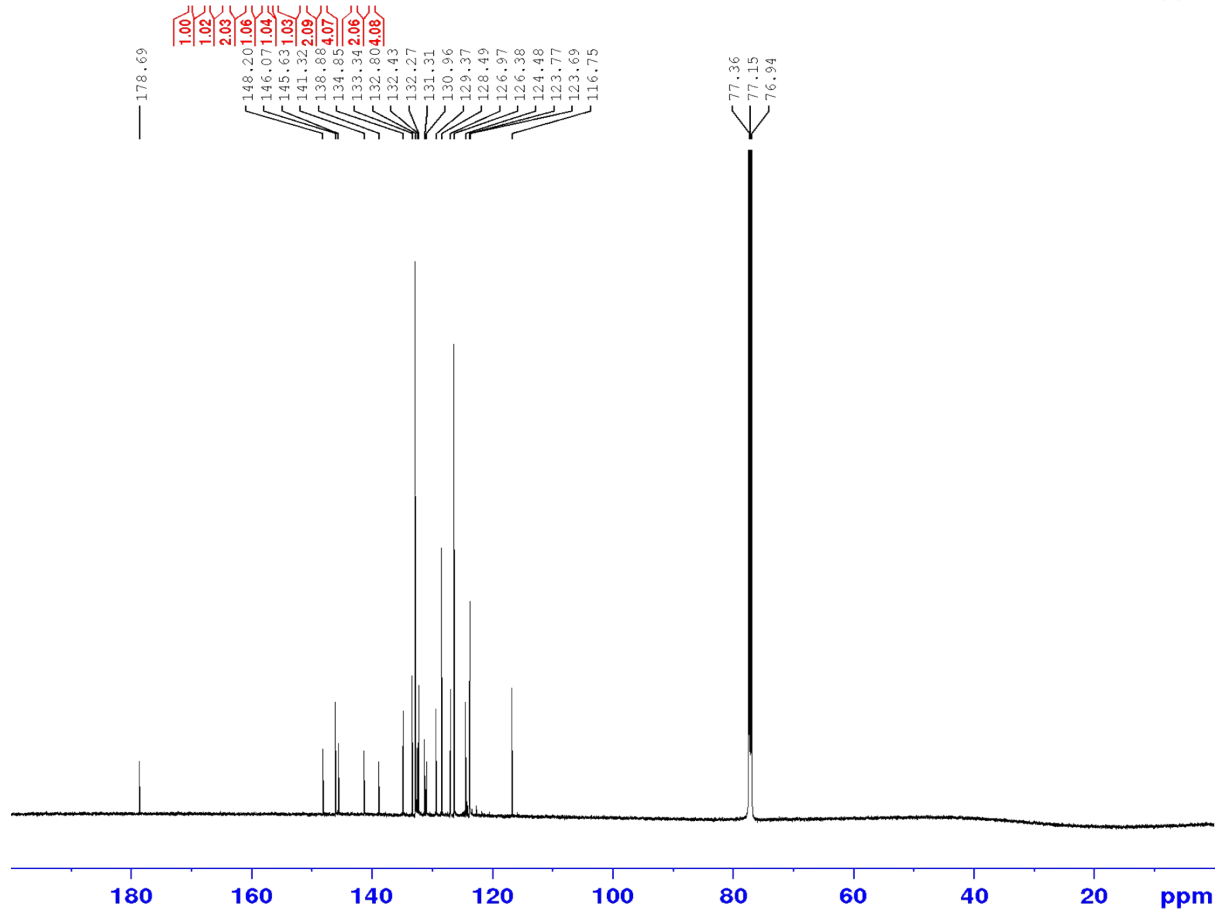
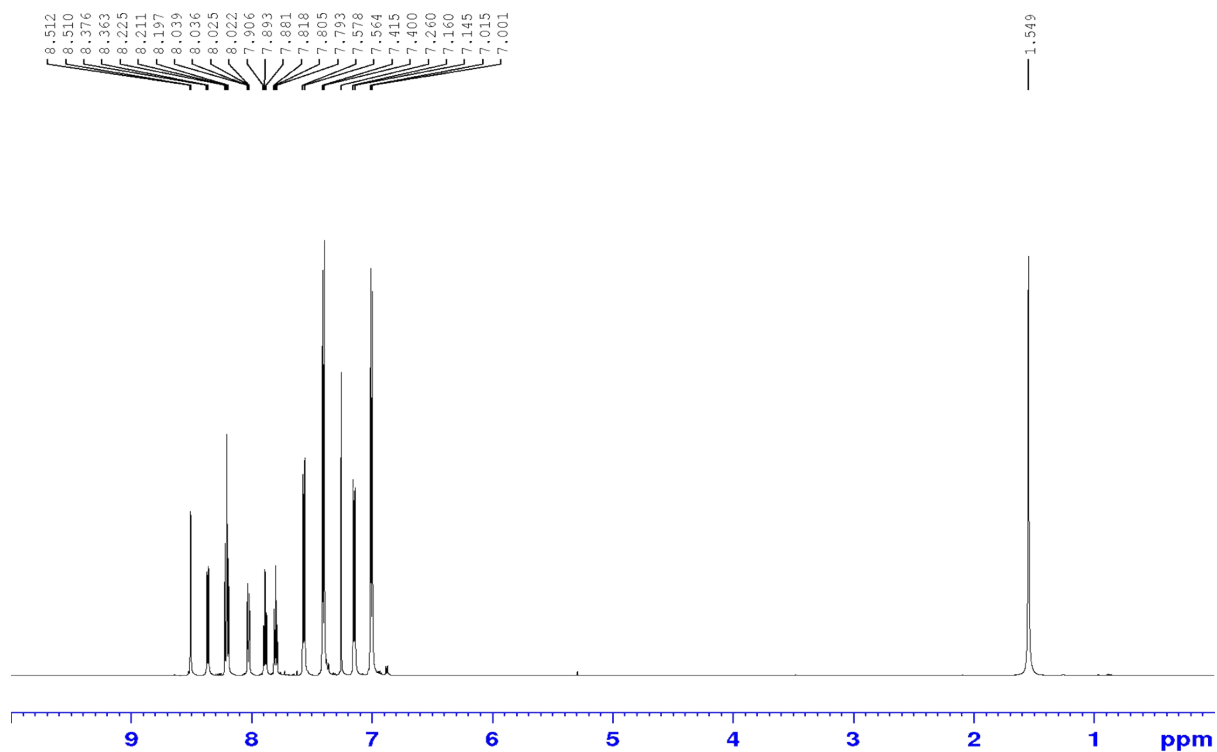
Fig. S5 FTIR spectra.

Fig. S6 Copies of ^1H and ^{13}C -NMR spectra.

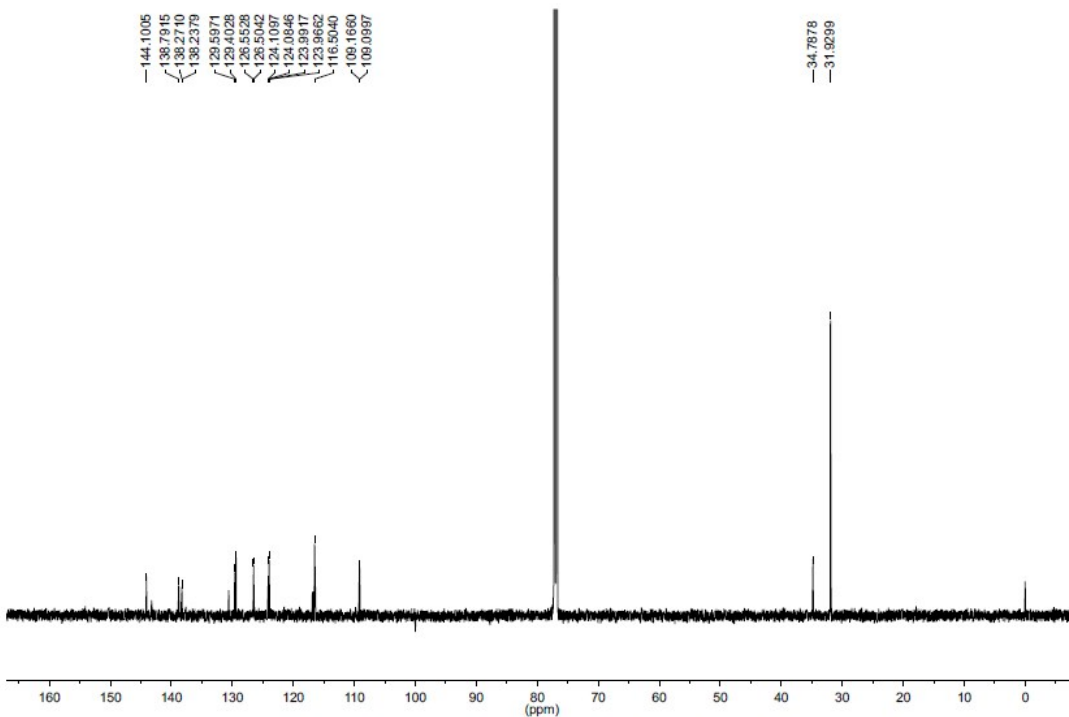
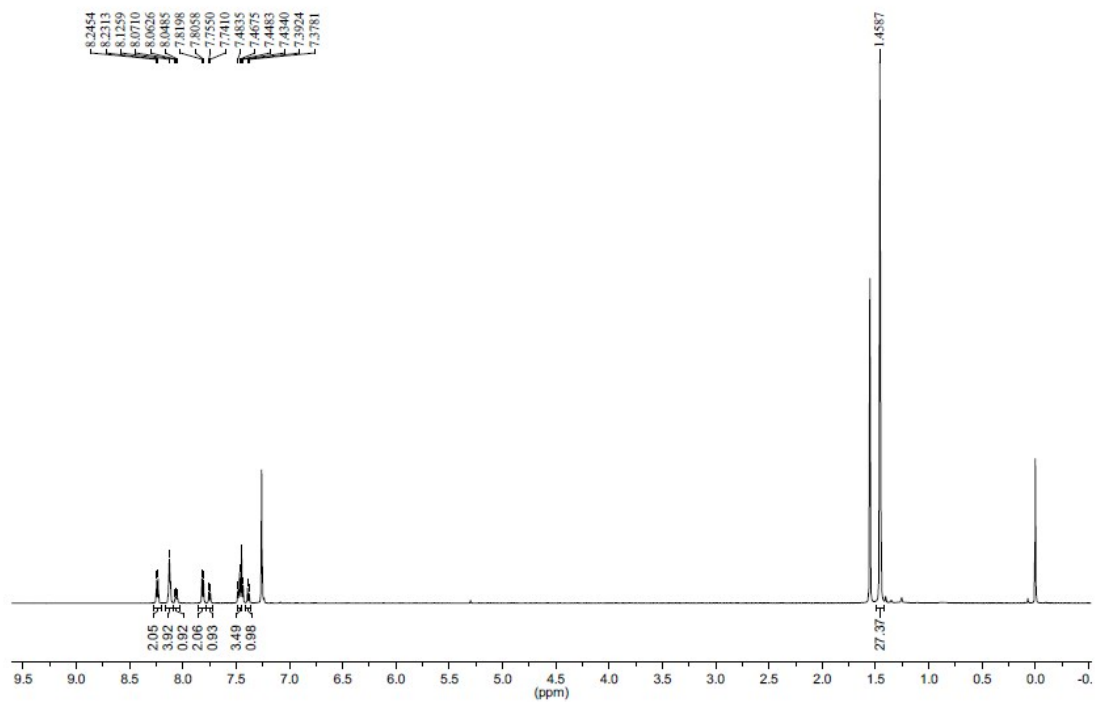
Compound 2



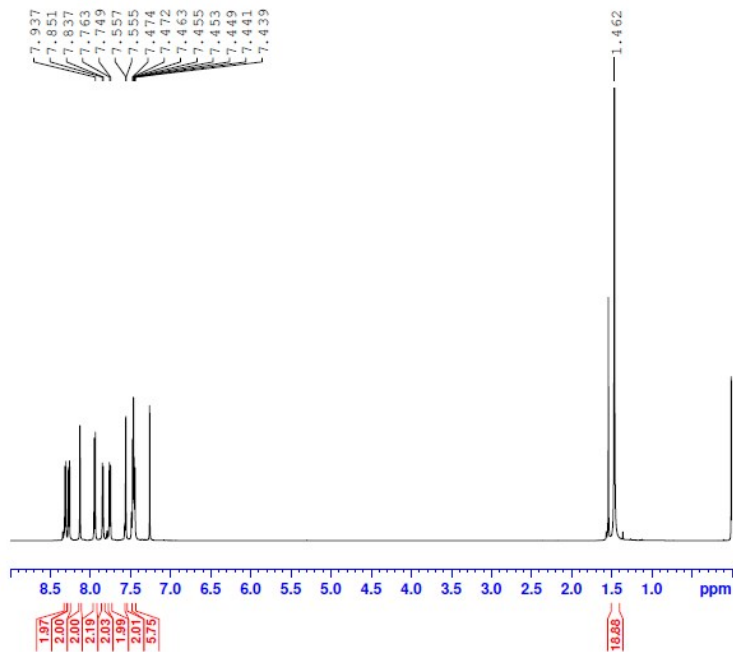
Compound M1



Compound 4



Compound M1

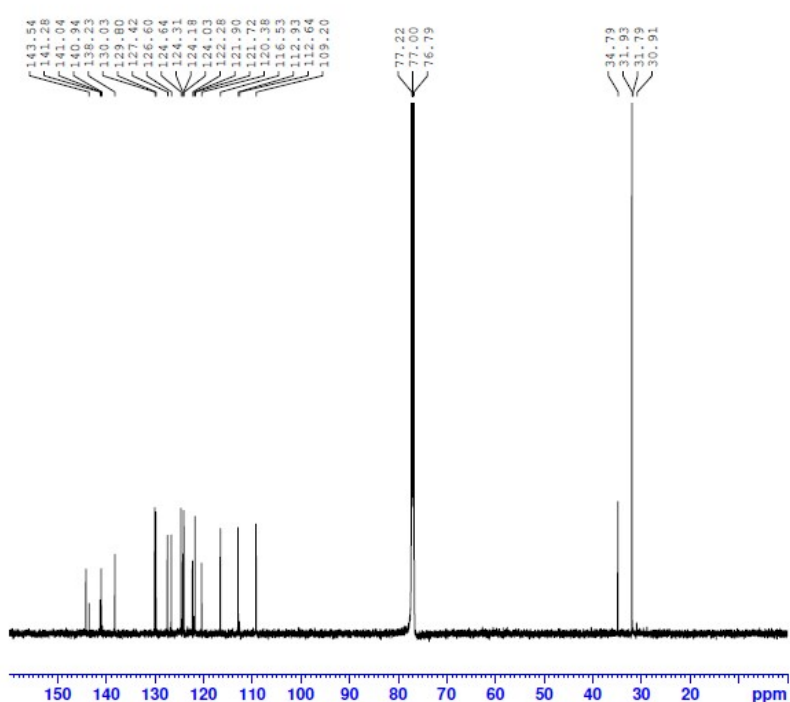


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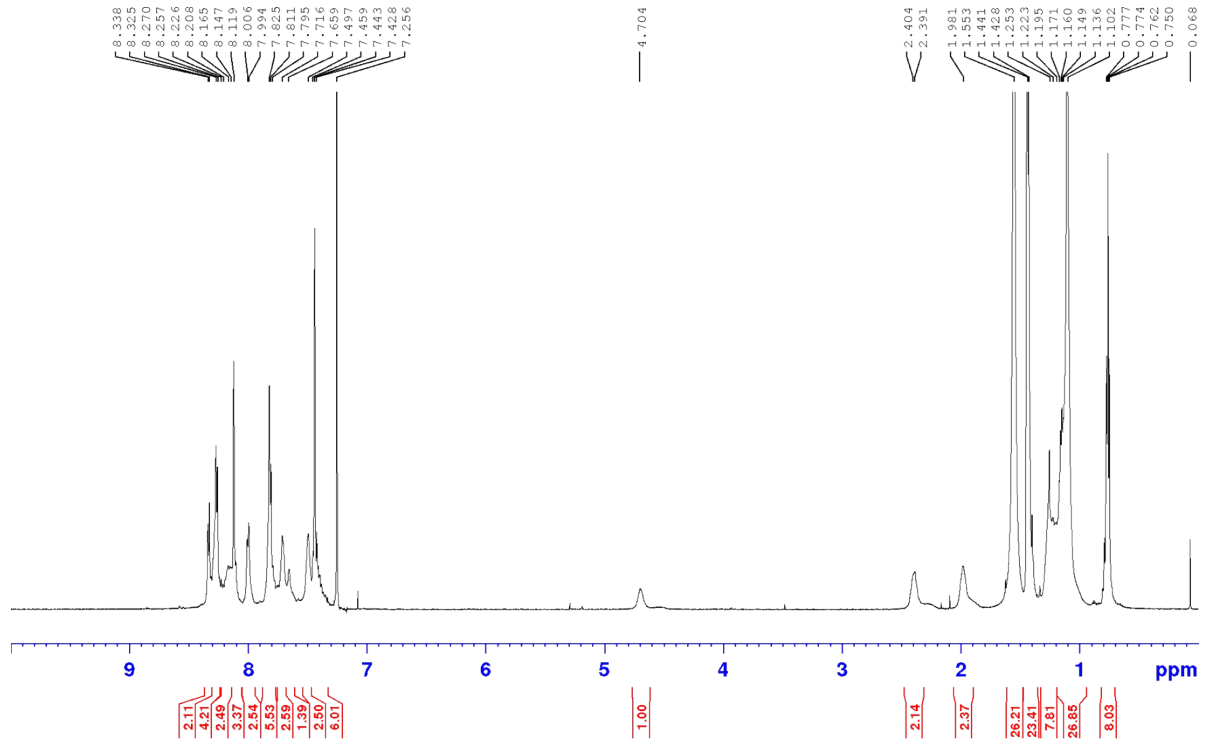
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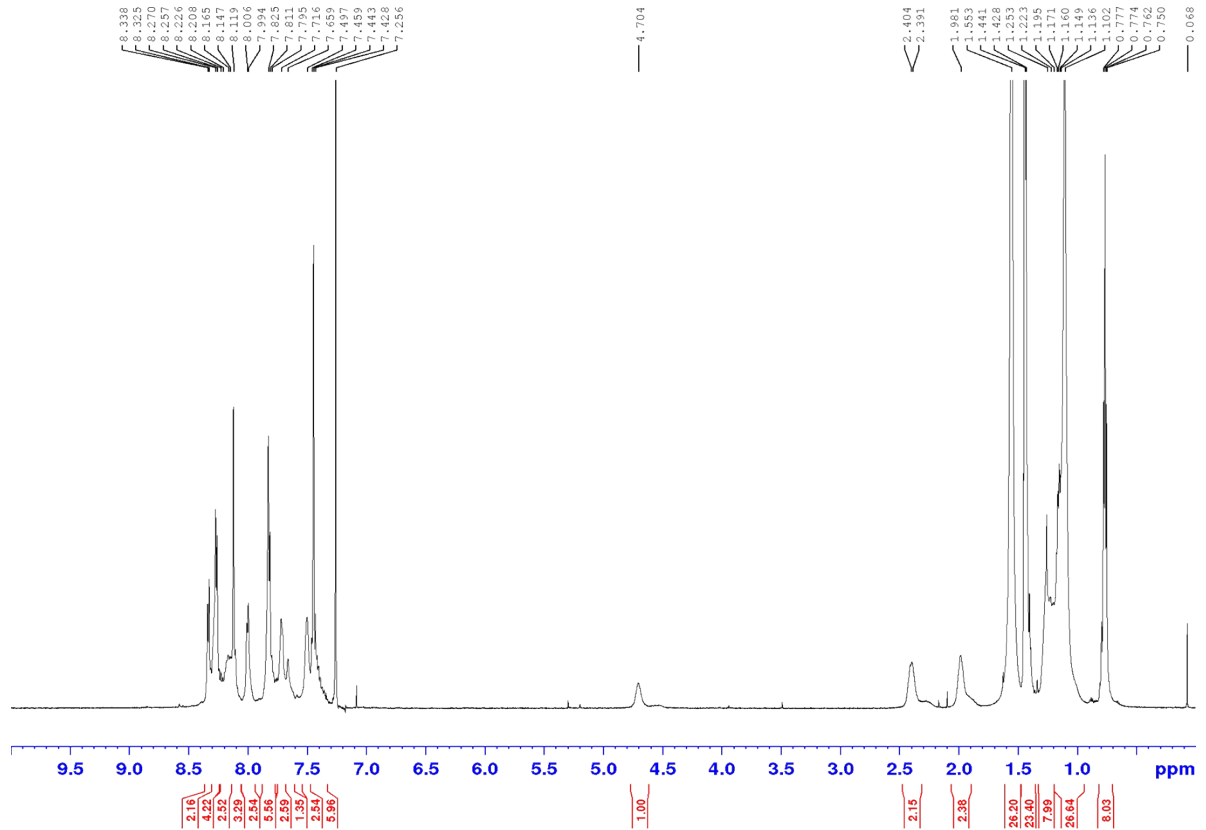
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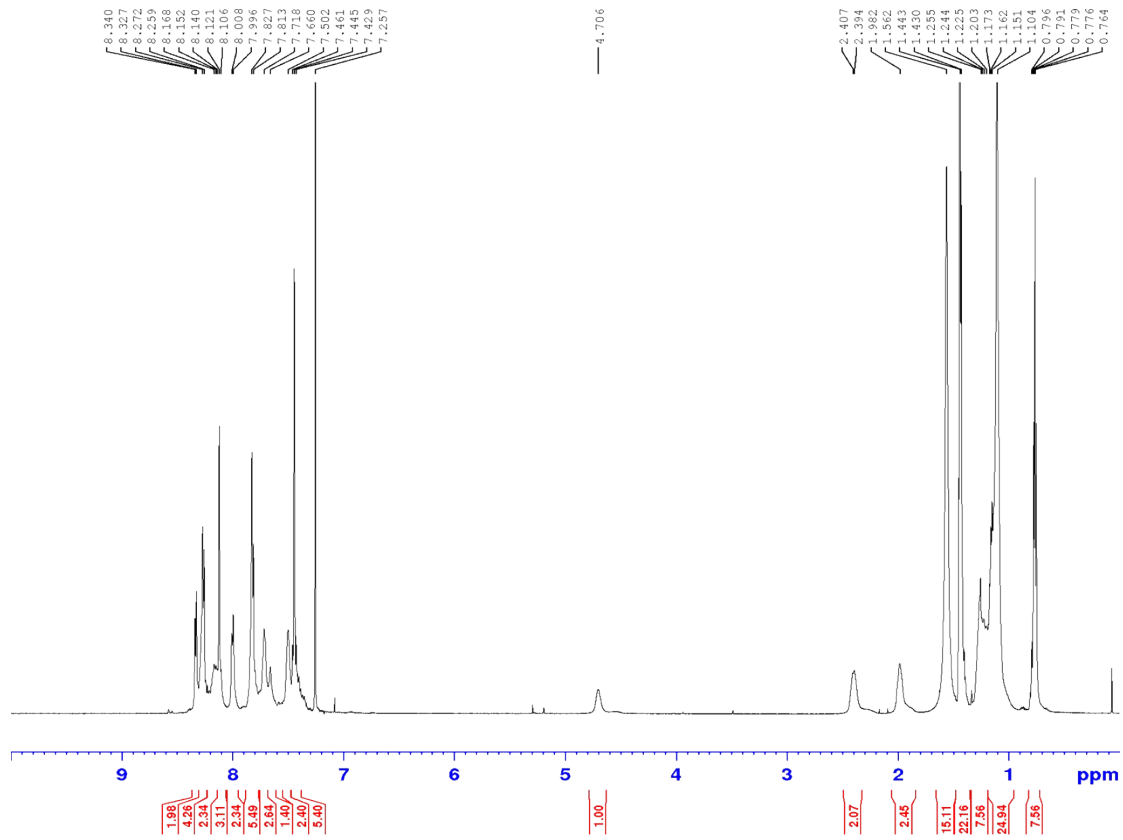
PCPSTT1



PCPSTT3



PCPSTT5



PCPSTT10

