

Supporting Information

For

White electroluminescence from Single Polymer System: Phenothiazine derivatives as red emissive dopant and Polyfluorene as blue host

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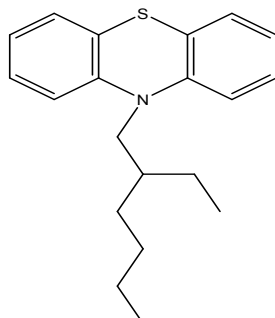
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Synthesis procedure for monomer and copolymers

Synthesis of 10-(2-ethyl hexyl)-10H-phenothiazine (PTZ-C₈H₁₇)

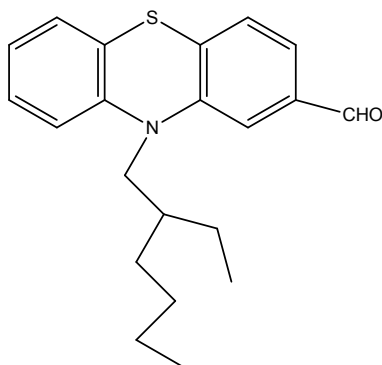


3-Bromooctane(16.58g, 100.36mmol), phenothiazine (10g, 50.18mmol), sodium hydroxide(20g, 500mmol), and dimethyl sulfoxide (DMSO) were placed in 500ml two neck round bottom flask, and then, this mixture was extracted with dichloromethane (DCM)/brine and then dried with sodium sulphate .The resulting liquid was purified by column chromatography. The product yield was 67% (9.53g).

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.16 (m, 4H), 6.97 (dd, *J* = 9.7, 3.8 Hz, 4H), 3.80 (s, 2H), 2.01 (s, 1H), 1.48 (dd, *J* = 15.3, 6.3 Hz, 2H), 1.35 (m, 4H), 0.95 (d, *J* = 5.6 Hz, 6H).

¹³C NMR(400 MHz, CDCl₃) δ 145.85,127.60,127.12,125.88,122.37,115.92,51.06,35.83,30.79,28.64,24.10, 23.12, 14.19 and 10.56

Synthesis of 10-(2-ethyl hexyl)-10H-phenothiazine-3-carbaldehyde (PTZ-CHO)



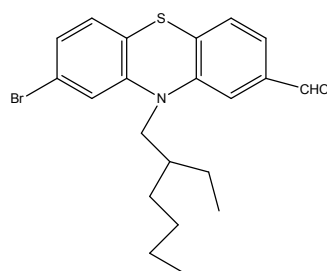
To a solution of 10-ethyl hexyl 10-H-phenothiazine (10g,31, 45mmol) and dry N,N-Dimethylformamide (DMF) (2.9 ml, 37.74mmol) in 1,2-dichloroethane 50 ml kept 0°C (ice water bath), POCl_3 (3.52ml, 37.74mmol) was added slowly. After the addition was complete the mixture was heated over night of reflux. The reaction mixture was quenched with water and extracted three times with chloroform. The combined organic fractions were washed with brine and dried over Na_2SO_4 . The solvent was removed under the reducing pressure and residue was purified by silica gel column chromatography using petroleum ether (P.E)-Ethyl Acetate (E.A) (8/2,V/v) as the eluent to give yellow liquid yield-90%.

^1H NMR (400 MHz, CDCl_3) δ 9.87 (s, 1H), 7.65 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.61 (d, $J = 1.9$ Hz, 1H), 7.16 (td, $J = 8.8, 1.4$ Hz, 2H), 6.98 (td, $J = 7.6, 1.0$ Hz, 1H), 6.92 (dd, $J = 10.0, 8.5$ Hz, 2H), 3.81 (m, 2H), 1.92 (dt, $J = 12.5, 6.4$ Hz, 1H), 1.46(m, 4H), 1.26 (m, 4H), 0.86 (d, $J = 7.3$ Hz, 6H).

^{13}C NMR (400 MHz, CDCl_3) δ 190.15, 151.53, 144.04, 131.12, 129.89, 128.76, 127.79, 127.49, 126.21, 124.93, 123.63, 116.61, 115.50, 51.46, 35.96, 30.56, 28.49, 23.91, 23.01,

13.99 and 10.45. Elemental analysis calculated (%) for $\text{C}_{21}\text{H}_{25}\text{NOS}$: C, 74.11; H, 7.35; N, 4.11; S, 9.4; O, 4.7; Found, C, 73.5; H, 7.0; N, 4.0; S, 9.5; O, 4.5. ESI mass calculated for $\text{C}_{21}\text{H}_{25}\text{NOS}$ 339.5; Found, 340

Synthesis of 7-bromo-10-(octyl-3-yl)-10H-phenothiazine-3-carbaldehyde (PTZ-Br)



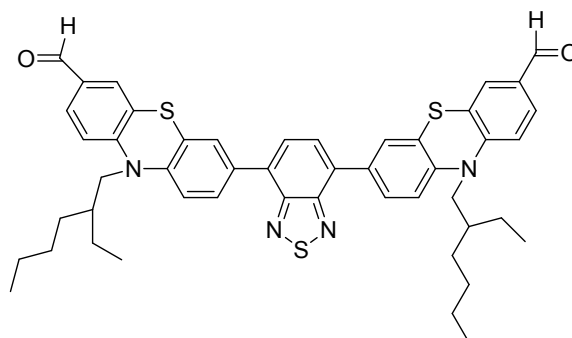
10-Ethyl hexyl 10H-phenothiazine 3-carbaldehyde (3.4g, 10mmol) and (0.5g, 12mmol) of NaOH were dissolved in the mixture of 40 ml of DCM and 45 ml of acetic acid. 10 ml of acetic acid containing (0.62ml, 12mmol) of bromine was added into the solution that was kept in an ice bath and then the mixture was taken out and stirred for 24h at room temp. 300ml of water was poured to stop the reaction and the mixture was extracted with DCM, then the product was purified by flash chromatography P.E/E.A-5:1V/v.

^1H NMR (400 MHz, CDCl_3) δ 9.81 (s, 1H), 7.67 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.60 (d, $J = 1.9$ Hz, 1H), 7.27 (dd, $J = 5.7, 4.0$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 1H), 6.75 (d, $J = 9.1$ Hz, 1H), 3.75 (d, $J = 7.3$ Hz, 2H), 2.17 (s, 10H), (1.28(m, 1H), 0.86 (td, $J = 7.4, 4.6$ Hz, 6H).

^{13}C NMR (400 MHz, CDCl_3) δ 190.00, 151.08, 143.26, 131.40, 130.24, 130.07, 130.03, 128.79, 127.20, 125.54, 117.72, 115.85, 115.69, 51.58, 35.96, 30.91, 30.52, 23.86, 22.98,

13.96 and 10.41. Elemental analysis calculated (%) for $\text{C}_{21}\text{H}_{24}\text{BrNOS}$; C,60.28; H, 5.78; Br, 19.10; N, 3.35; S, 7.66; O, 3.82; Found; C,61.0; H, 5.5; Br, 19.0; N, 3.5; S, 7.5; ESI mass calculated for $\text{C}_{21}\text{H}_{24}\text{BrNOS}$ 418; Found, 418.3

Synthesis of 7,7'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(10-(2-ethylhexyl)-10H-phenothiazine-3-carbaldehyde) (BTPTZ-CHO)



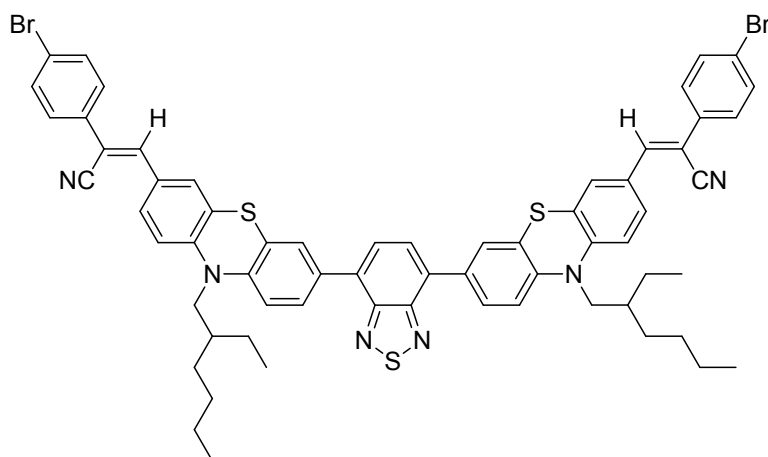
(1.07 grams 1.2mmol) of 7-bromo-10-(octyl-3-yl)-10H-phenothiazine-3-carbaldehyde and 2,1,3-benzothiadiazole 4,7-diboronic ester (0.5g, 0.6mmol) was taken in 2 neck 100ml R.B and dissolved in Tetrahydrofuran (THF), 20 ml of 2% k_2CO_3 solution was added. The temperature was reached to 60⁰c then $Pd(PPh_3)_4$ (138 mg, 0.24) was added to the reaction mixture under nitrogen atmosphere after that again 10 ml of THF was added. The reaction temperature 85⁰c was maintained after reaction completed the reaction mixture was poured into 250ml beaker containing 100ml distilled water and extracted with chloroform. The crude product was separated by column chromatography by using 10% E.A and hexane

Chemical shift; ¹H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 2H), 7.75 (d, $J = 20.9$ Hz, 4H), 7.69 – 7.53 (m, 6H), 6.95 (dd, $J = 32.4, 6.2$ Hz, 4H), 3.79 (d, 4H), 1.93 (m, 2H), 1.56-1.22 (m, 16H), 0.81 (m, 12H).

¹³C NMR (400 MHz, $CDCl_3$) δ 190.15, 153.85, 151.03, 144.26, 132.79, 131.51, 131.30, 130.01, 128.85, 128.47, 128.18, 127.36, 125.94, 125.10, 116.50, 115.65, 51.54, 36.02, 30.60, 28.52, 23.91, 23.08, 14.05 and 10.48.

Elemental analysis calculated (%) for $C_{48}H_{49}N_4O_2S_3$: C, 71.16; H, 6.10; N, 6.92; S, 11.87; O, 3.95; Found C, 71.0; H, 6.2; N, 7.0; S, 11.9; O, 4.0. ESI mass calculated for $C_{48}H_{49}N_4O_2S_3$ 810.12; Found, 810.

Synthesis of 3,3'-(7,7'-(benzo[1,2,5 thiadiazole-4,7 diyl]bis(10-octyl-10H-phenothiazine-7,3-diyl)bis(2-(4-bromo phenyl)acrylonitrile) (BTZPZP)



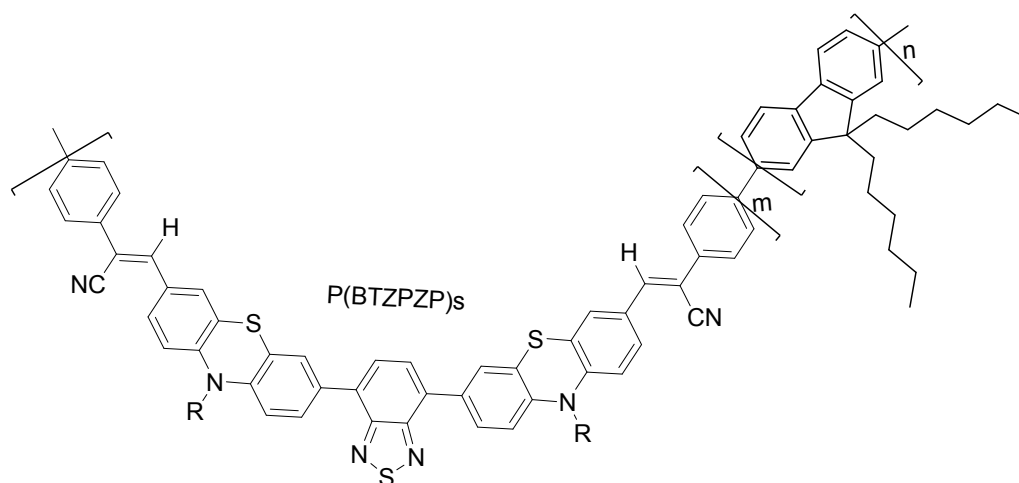
7,7'-(benzoc1,2,5thiadiazole-4,7-diyl)bis(10-octyl-10H-phenothiazine-3-carbaldehyde) (1g, 0.59mmol), 4-bromo phenyl acetonitrile (0.68g, 1.77mmol) and potassium tertiary but oxide (396mg, 1.77) taken 100ml of single necked R.B. These all reactants were dissolved in 30 ml of methanol and 10 ml of THF, the reaction mixture was reflux for 12 hours. After that precipitate was formed. This precipitate was filter and washed with 2 to 3 times with ethanol. After filtration compound was dried by using vaccum oven.

Chemicalshift;¹H NMR (400 MHz, CDCl₃) δ 7.85(t, 4H), 7.80 (d, 2H), 7.72 (s, 2H), 7.62 (d, 2H), 7.52 (q, 8H), 7.35 (s, *J* = 18.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.70 (d, 4H), 2.0 (m, 2H), 1.4 – 1.5 (m, 4H), 1.25-1.33 (m, 12H), 0.90 (m, *J* = 9.5, 6.3 Hz, 12H).

¹³C NMR (400 MHz, CDCl₃) δ 153.86, 147.52, 144.53, 141.13, 133.72, 132.43, 132.34, 132.15, 131.34, 130.54, 128.92, 128.66, 128.39, 128.10, 127.93, 127.24, 125.63, 124.90, 122.91, 118.12, 116.20, 115.93, 107.39, 51.24, 31.97, 30.66, 29.73, 29.70, 29.41, 28.58, 23.96, 23.13, 22.75, 14.21, 14.11, 10.54

Elemental Analysis, calculated (%): C, 76.3; H, 5.76; N, 8.35; S, 9.54: Found (%): C, 76.0: H, 9.0: N, 8.2: S, 9.3 MALDI mass calculated m/z: Calculated for C₆₄H₅₈Br₂N₆S₃: 1164, found: 1166.

Polymerization



A series of copolymers were synthesised by using Suzuki poly condensation reaction using different composition of feed ratio of the BTZPZP monomer and co-monomers (Different feed ration in Table S1). The obtained conjugated copolymers with different BTZPZP to fluorene ratios and their M_n and poly dispersity index (PDI) values are in Table S1. The corresponding copolymers labelled as BTZPZP 0.125, BTZPZP 0.25, BTZPZP 0.5, BTZPZP 1, BTZPZP 2.5, and BTZPZP 5 (Scheme 1). In a representative controlled synthetic procedure (23.3mg,0.02mmol) of BTZPZP along with (180 mg,0.38mmol) of 9,9-dihexyl -2,7-dibromofluorene and (200mg, 0.4mmol) of 9,9-dihexylfluorene -2,7-diboronic acid (1,3-propane diol) ester was dissolved in 50ml of (THF). To the above mixture of reactant, (25 ml) 2% potassium carbonate solution was added; the resulting mixture was degassed with nitrogen on heating when the reaction mixture temperature reached to 50⁰ C, catalytic amount of Tetrakis triphenyl phosphine palladium (0) was added to the reaction mixture under the nitrogen condition the mixture of the content was refluxed with constant stirring for 72 hours. The resulting mixture was concentrated under vacuum and redissolved in chloroform. The chloroform solution was washed with 3N HCL solution and water. The organic layer was separated and concentrated through rotary evaporator to get crude product of copolymer **BTZPZP-5 Copolymer**. The resulting crude product was purified through reprecipitation from the concentrated chloroform solution with methanol to get red precipitate, dried and weighed. Yield 69%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.65-2.05 (m 4H), 7.3 (m, 5H), 7.42 (m, 7H), 7.55-7.65 (m, 14H) and 7.70-7.80 (m, 5H), 2.0-1.78(m, 20H), 0.7-1.5(m-110H) Elemental Analysis, calculated (%): C, 88.43; H, 9.10; N, 1.14; S, 1.31.

Found (%):C, 88.22; H, 9.05; N, 1.08; S, 1.25

BTZPZP-2.5 Copolymer: (11.27mg, 0.01mmol) of BTZPZP along with (180mg, 0.38mmol) of 9,9'-dihexyl -2,7-dibromofluorene and (200mg, 0.4mmol) of 9,9-dihexyl-2,7-diboronic acid (1,3-propane diol) ester were used in the polymerisation, Yield 78%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.62-2.1 (m, 140H), 7.25 (m, 4H), 7.41 (m, 6H), 7.45-7.60 (m, 8H) and 7.70-7.80 (m, 10H), Elemental analysis, Calculated (%): C, 89.36; H, 9.36; N, 0.60; S, 0.68.

Found (%): C, 89.12; H, 9.25; N, 0.57; S, 0.63.

BTZPZP-1 Copolymer: (5.77mg, 0.049mmol) of BTZPZP along with (243mg, 0.495mmol) of 9,9'-dihexyl -2,7-dibromofluorene and (250mg, 0.5mmol) of 9,9-dihexyl-2,7-diboronic acid (1,3-propane diol) ester were used in the polymerisation, Yield 74%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.67-2.15 (m, 148H), 7.27 (m, 2H), 7.42 (m, 6H), 7.5-7.65 (m, 10H) and 7.75-7.85 (m, 14H), Elemental analysis, Calculated (%): C, 89.94; H, 9.52.

Found (%): C, 89.79; H, 9.42

BTZPZP-0.5 Copolymer: (2.33mg, 0.02mmol) of BTZPZP along with (195.8mg, 0.4mmol) of 9,9'-dihexyl -2,7-dibromofluorene and (250mg, 0.5mmol) of 9,9-dihexyl-2,7-diboronic acid (1,3-propane diol) ester were used in the polymerisation, Yield 76%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.63-2.08 (m, 164H), 7.35 (t, 2H), 7.40 (t, 4H), 7.55-7.6 (m, 5H) and 7.70-7.80 (m, 8H), Elemental analysis, Calculated (%): C, 90.1; H, 9.58. Found (%): C, 90.15; H, 9.62

BTZPZP-0.25 Copolymer: (1.16mg, 0.001mmol) of BTZPZP along with (196.3mg, 0.399mmol) of 9,9'-dihexyl -2,7-dibromofluorene and (200mg, 0.4mmol) of 9,9-dihexyl-2,7-diboronic acid (1,3-propane diol) ester were used in the polymerisation, Yield 69%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.56-2.10 (m, 180H), 7.27 (t, 8H), 7.42 (t, 6H), 7.57-7.67 (m, 10H) and 7.72-7.80 (m, 12H), Elemental analysis, Calculated (%): C, 90.25; H, 9.60.

Found (%): C, 90.37, H, 9.62

BTZPZP-0.125 Copolymer: (0.73mg, 0.0006mmol) of BTZPZP along with (245.6mg, 0.499mmol) of 9,9'-dihexyl-2,7-dibromofluorene and (250mg, 0.5mmol) of 9,9-dihexyl-2,7-diboronic acid (1,3-propane diol) ester were used in the polymerisation, Yield 74%.

¹H NMR (CDCl₃, 400MHz, ppm): δ0.55-2.2 (m, 220H), 7.32 (t, 12H), 7.42 (t, 6H), 7.55-7.65 (m, 12H) and 7.70-7.80 (m, 18H), Elemental analysis, Calculated (%): C, 90.30; H, 9.6. Found (%): C, 90.25, H, 9.58

Table S1. Feed ratio, composition and GPC data of copolymers

Polymer	Feed ratio ^a			Calculated values	^b Mw/Mn/PDI
	BTZPZP	M	N		
BTZPZP 0.125	0.00125	0.50	0.49875	0.00105	5578/4950/1.13
BTZPZP 0.25	0.0025	0.50	0.4975	0.00213	4655/4412/1.05
BTZPZP 0.5	0.005	0.50	0.495	0.00439	9265/6343/1.46
BTZPZP 1.0	0.01	0.50	0.49	0.00941	12990/7228/1.80
BTZPZP 2.5	0.025	0.50	0.475	0.0219	8799/6502/1.35
BTZPZP 5.0	0.05	0.50	0.45	0.0469	8434/6350/1.43

^a BTZPZP, mole fraction of BTZPZP; M, mole fraction of 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) ester; N, mole fraction of 9,9-Dihexyl-2,7-dibromofluorene. ^b Mw, Weight Averaged molecular weight; Mn, number averaged molecular weight; PDI, Polydispersity Index.

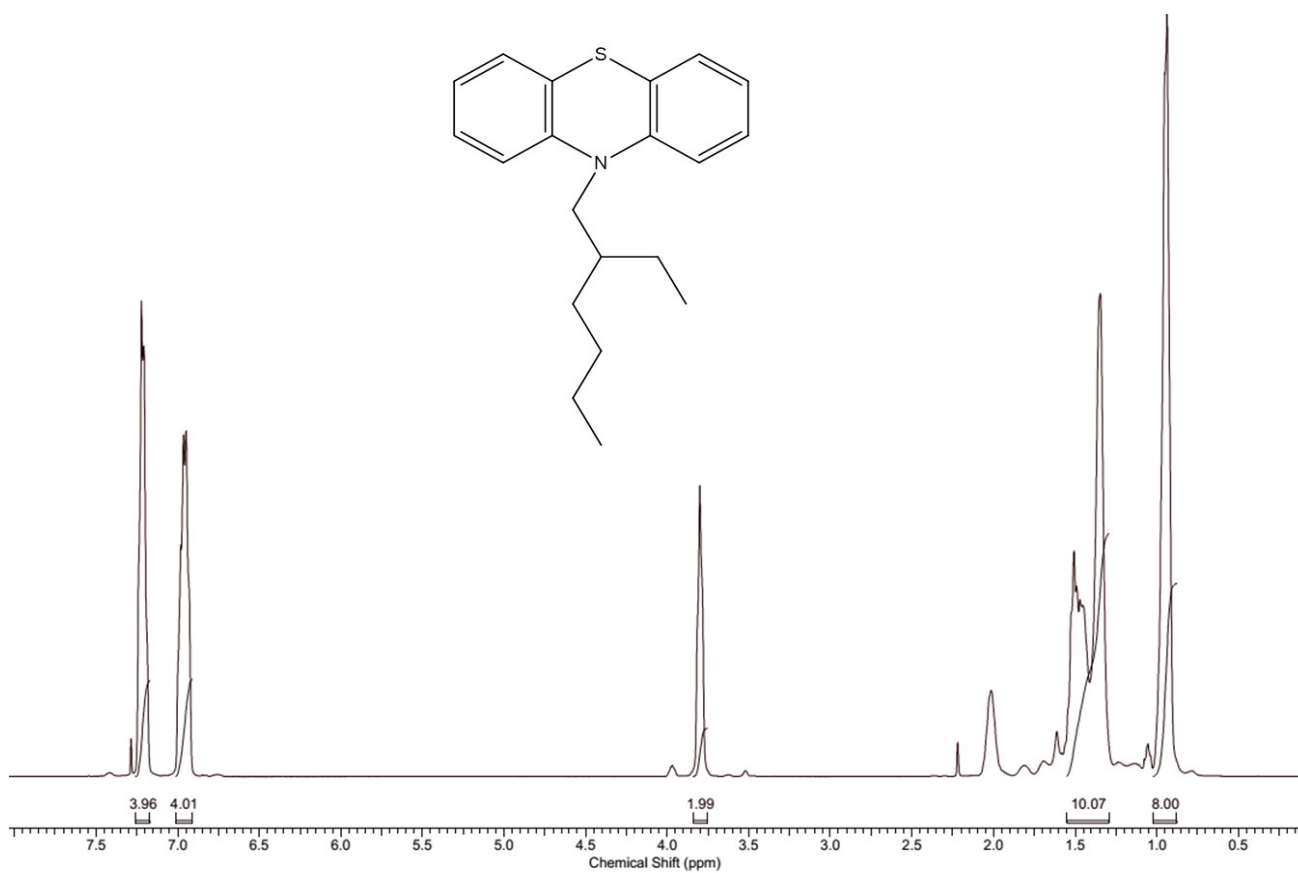


Figure S1-H ¹H NMR spectrum of PTZ-C₈H₁₇

Figure S2-C ¹³C NMR spectrum of PTZ-C₈H₁₇

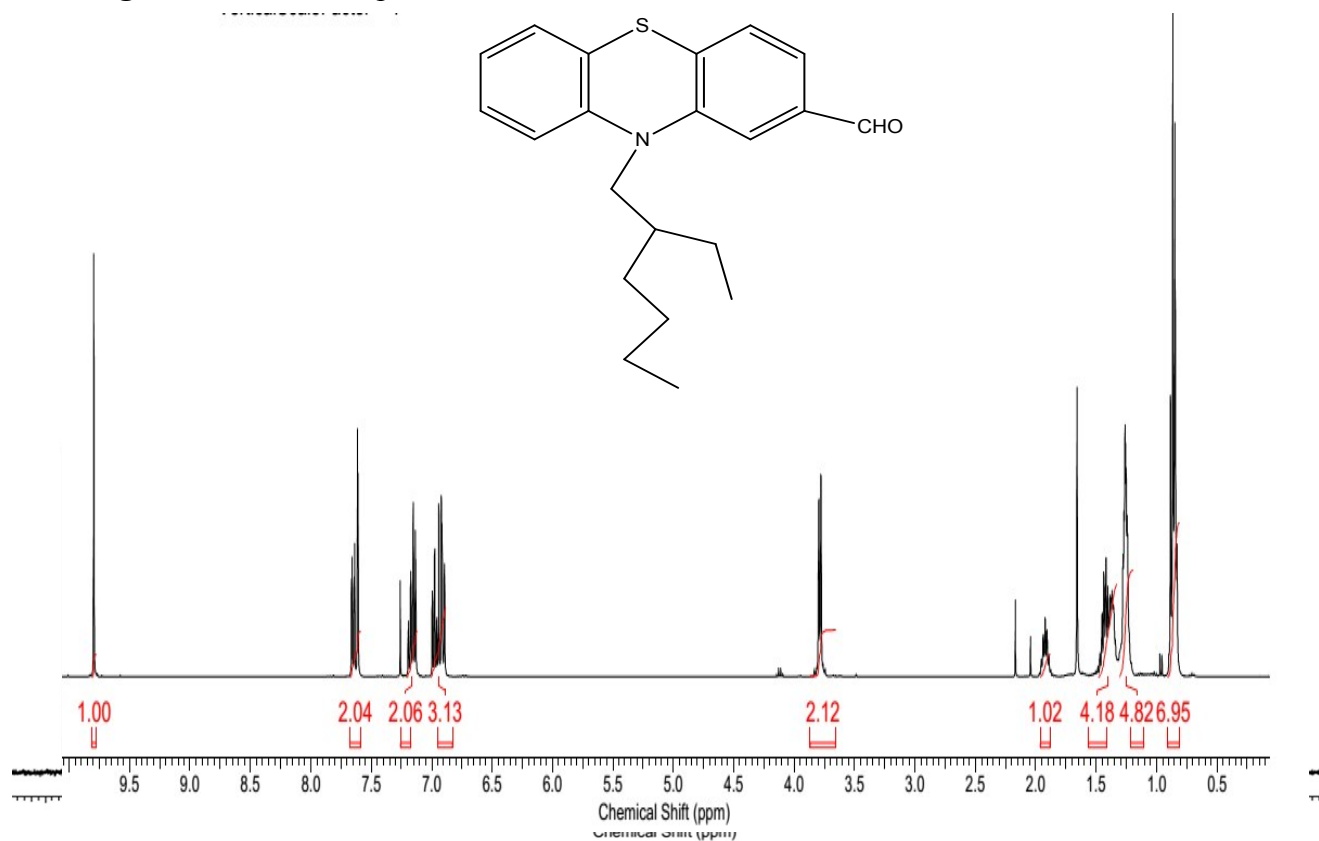


Figure S3-H ^1NMR spectrum of PTZ-CHO

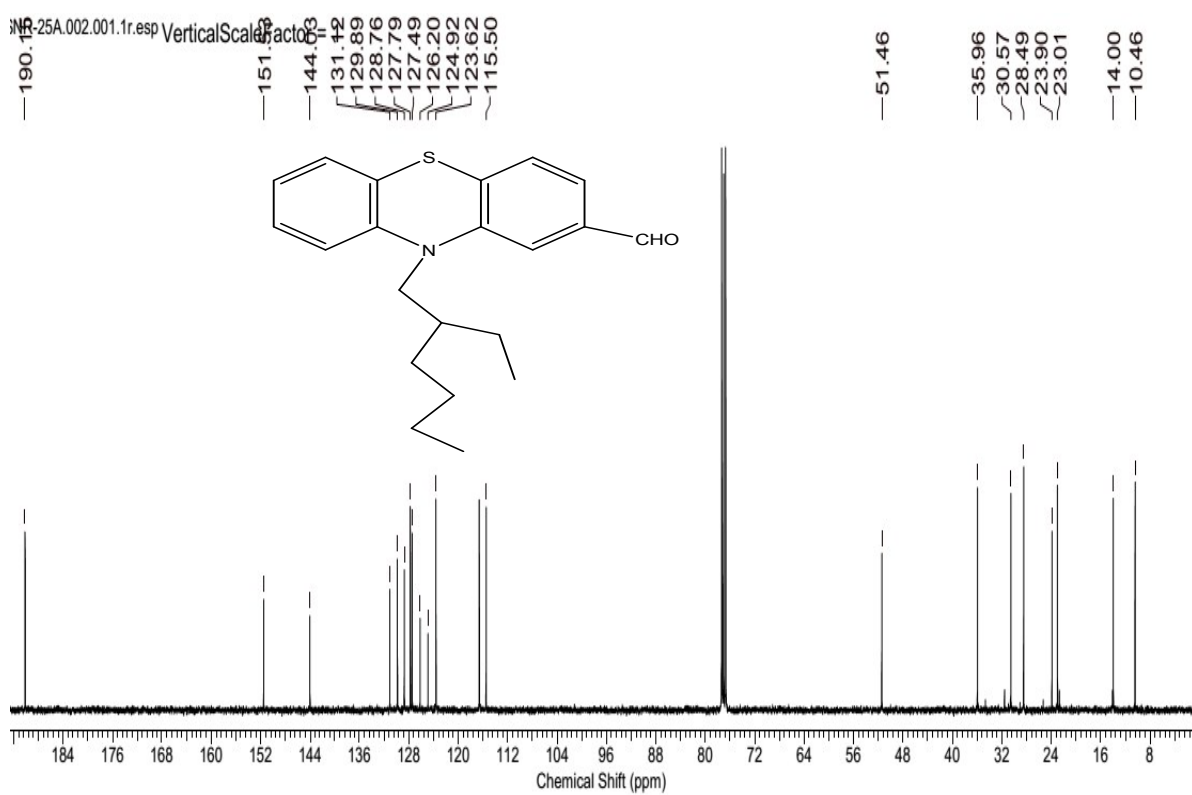


Figure S4-C ^{13}C NMR spectrum of PTZ-CHO

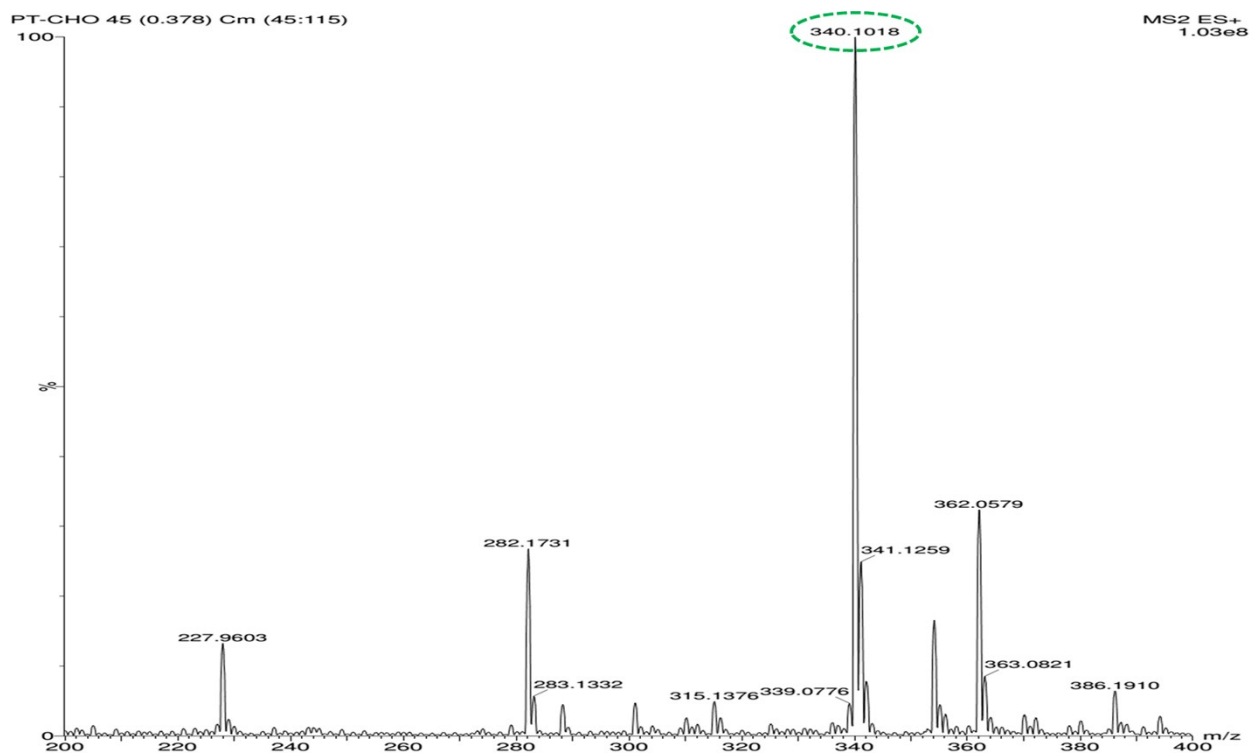


Figure S5- ESI mass spectrum of PTZ-CHO

5NR-26Z.001.001.1r.esp VerticalScaleFactor = 1

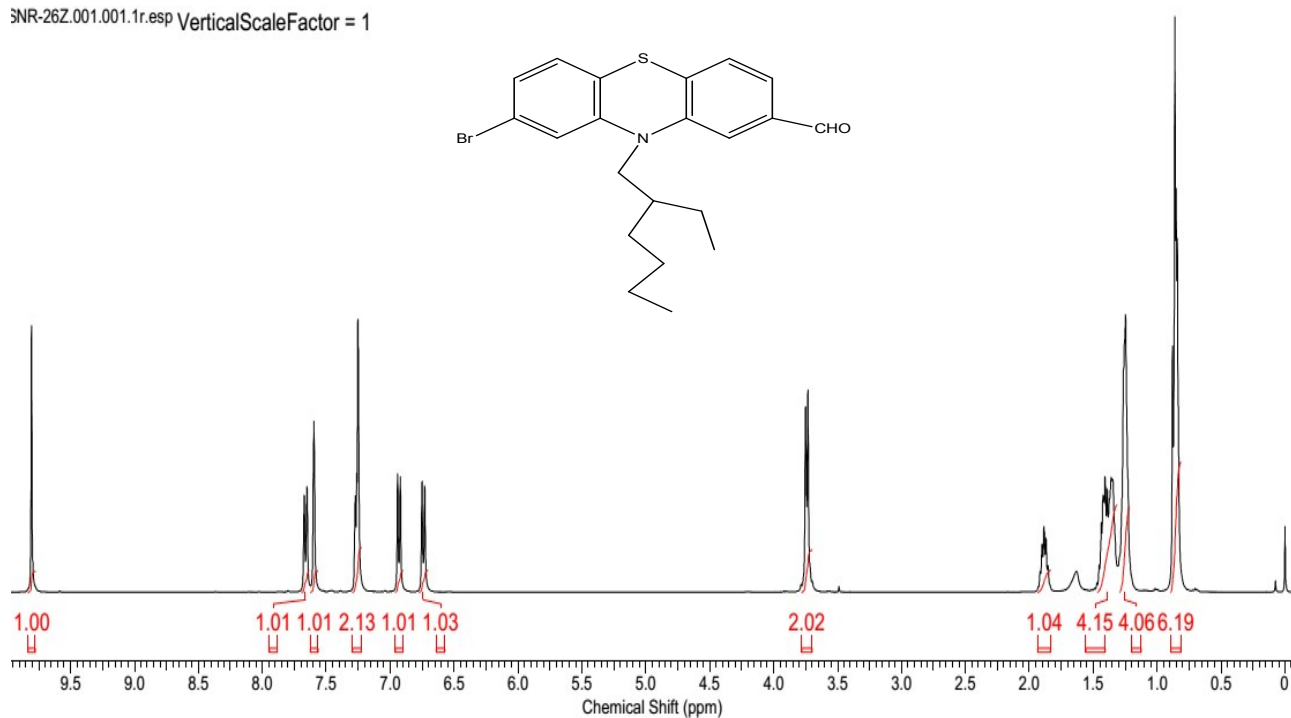


Figure S6-H ^1H NMR spectrum of PTZ-Br

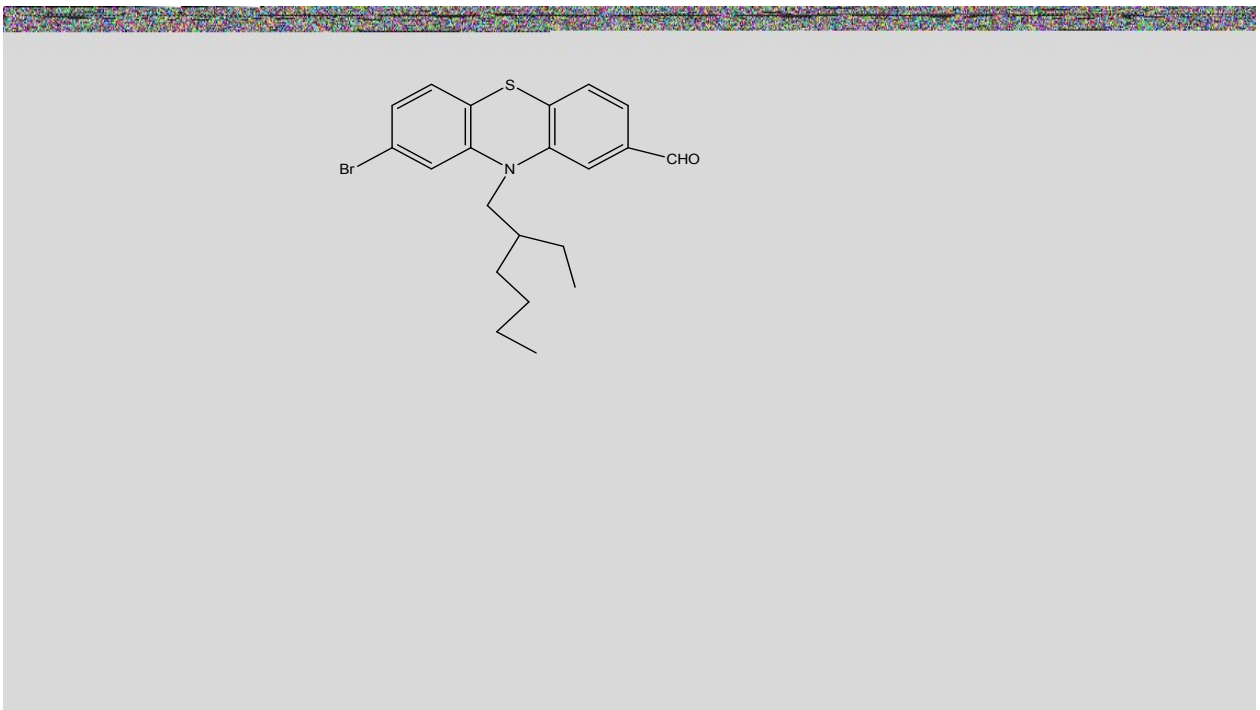


Figure S7-C ^{13}C NMR spectrum of PTZ-Br

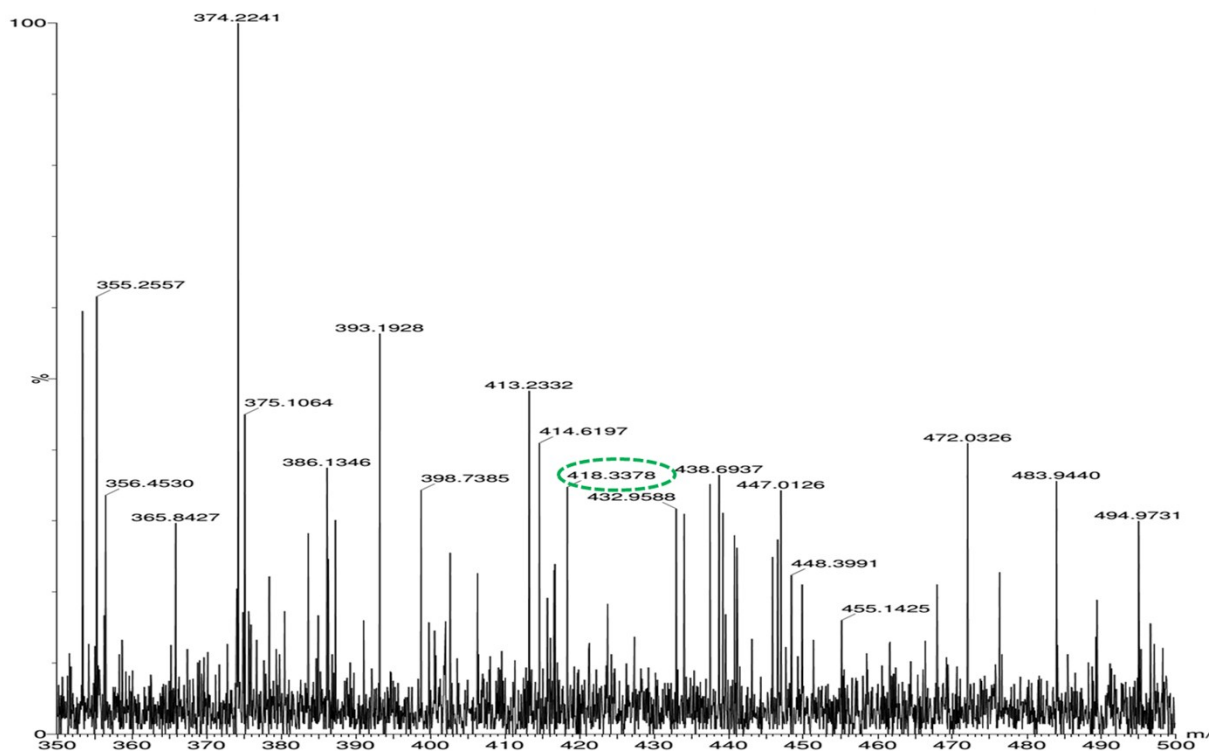


Figure S8- ESI mass spectrum of PTZ-Br

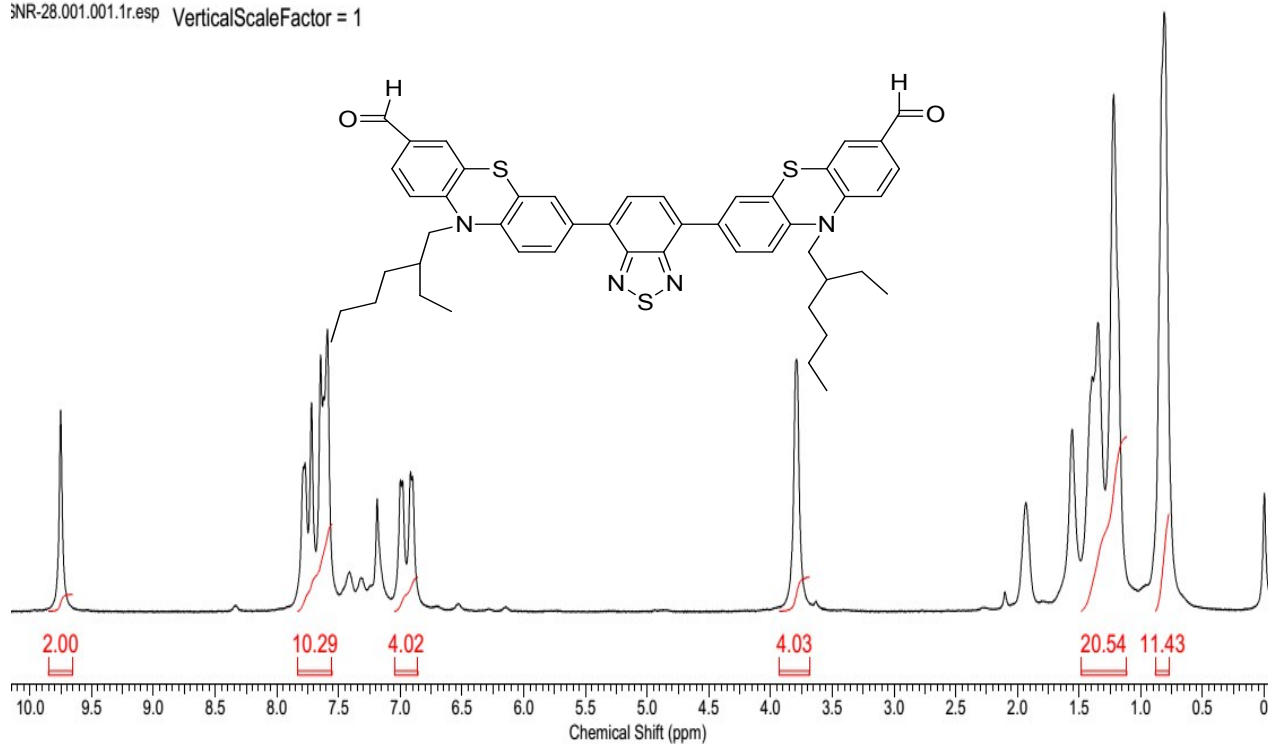


Figure S9-H ¹H NMR spectrum of BTPTZ-CHO

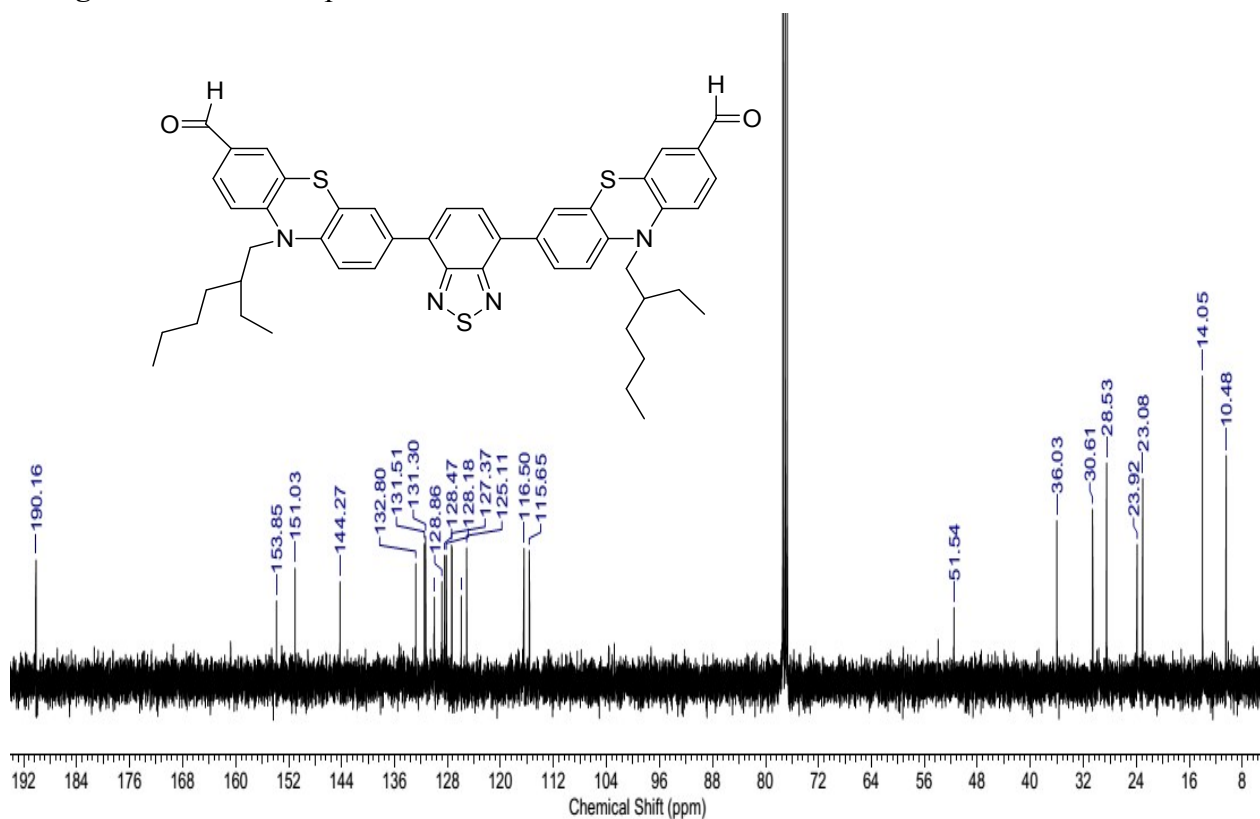


Figure S10-C ¹³C NMR spectrum of BTPTZ-CHO

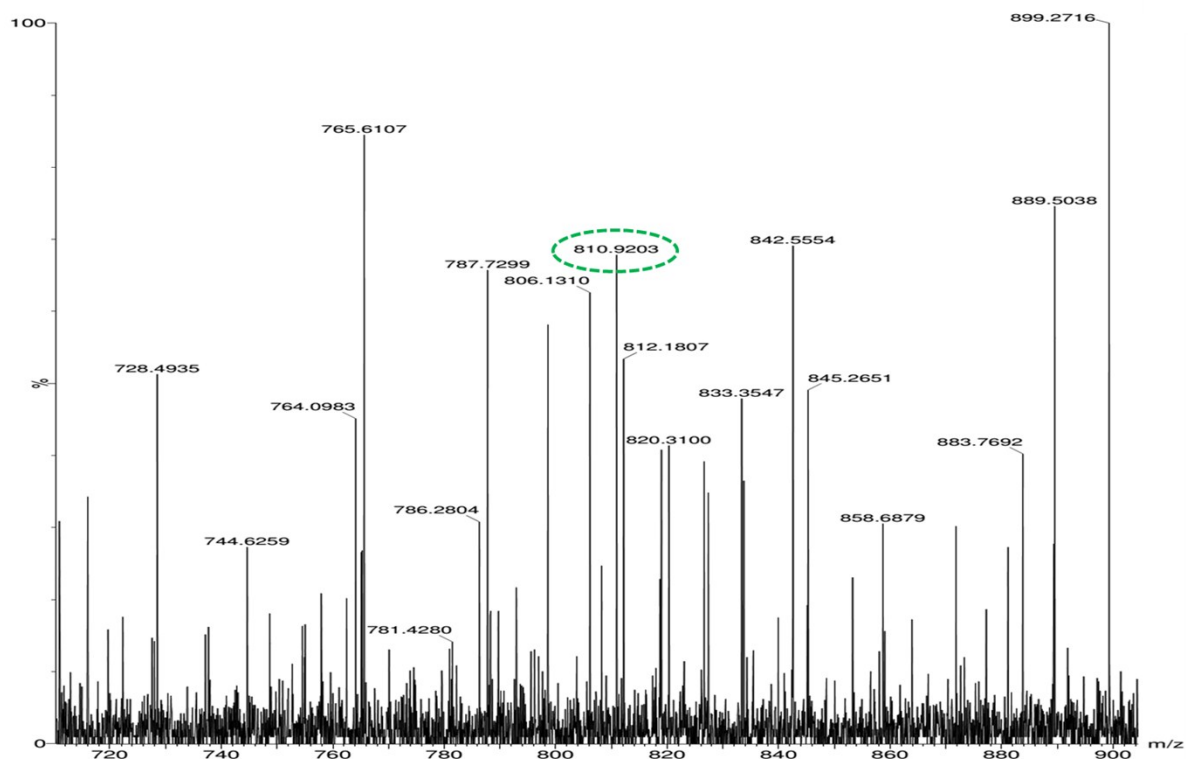


Figure S11-ESI mass spectrum of BTPTZ-CHO

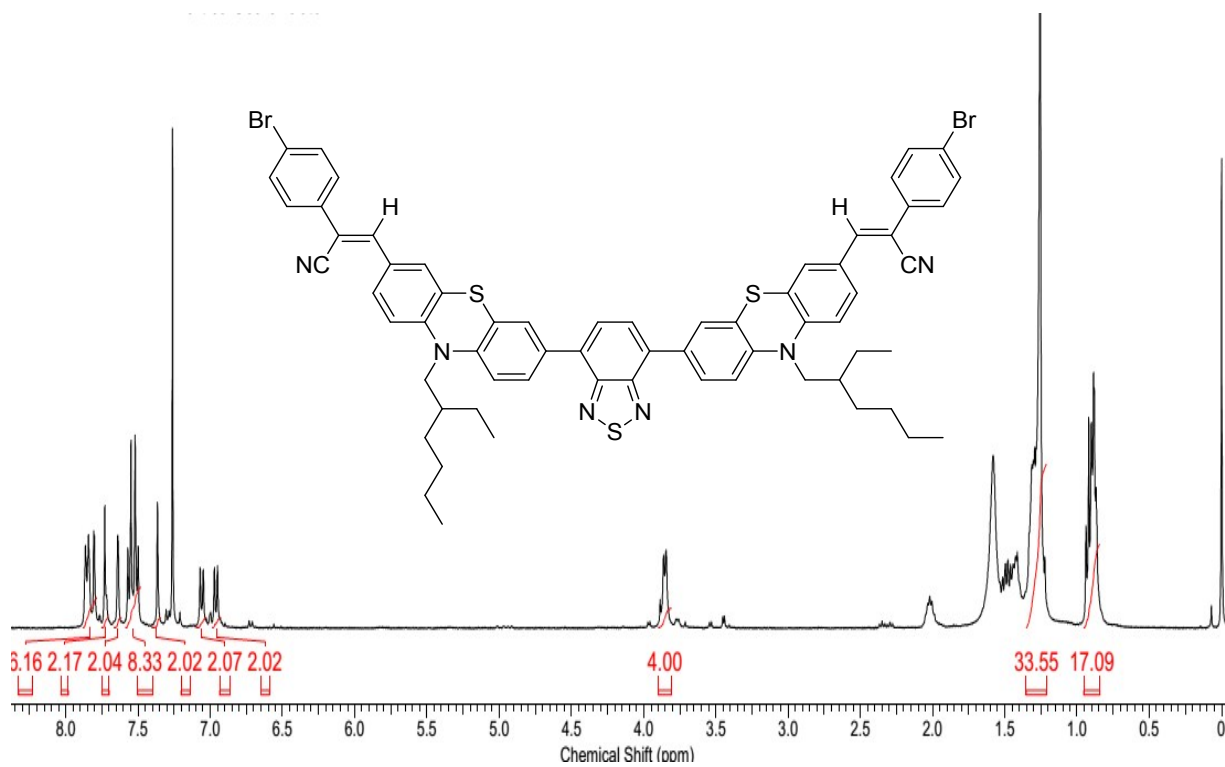


Figure S12-¹H NMR spectrum of BTZPZP

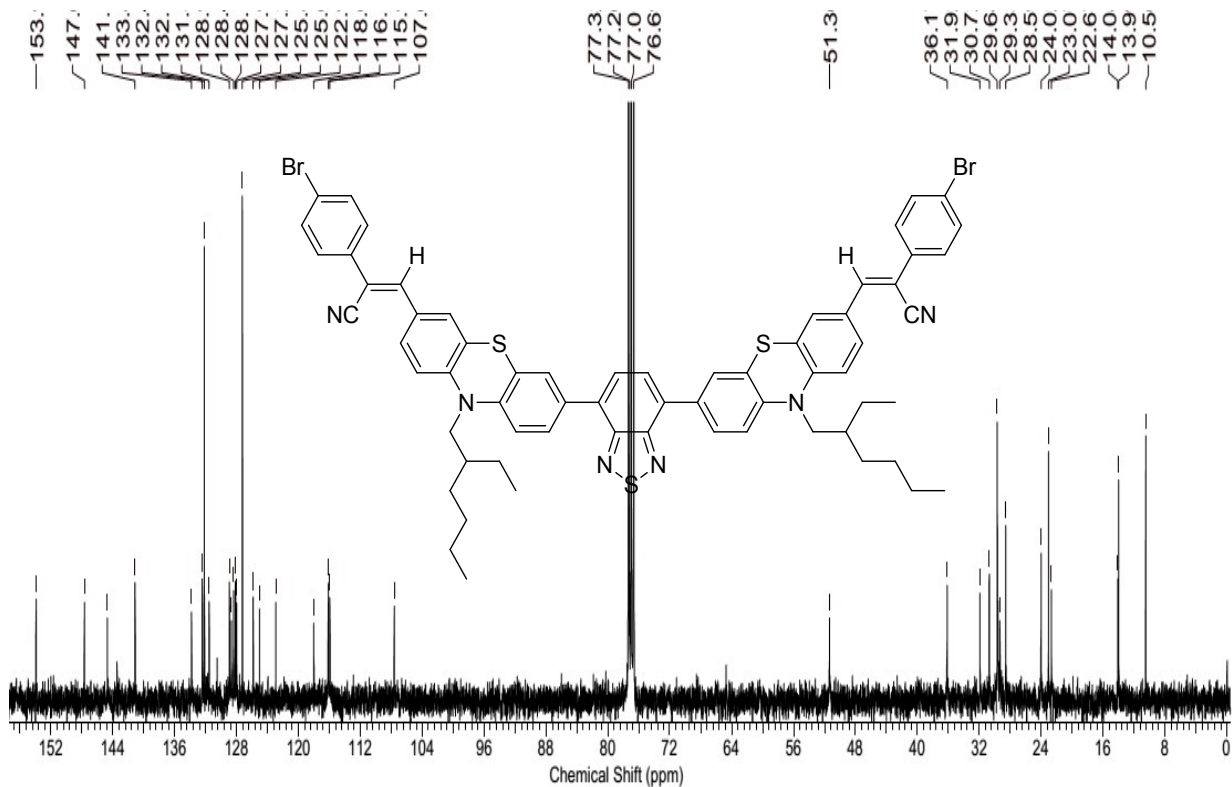
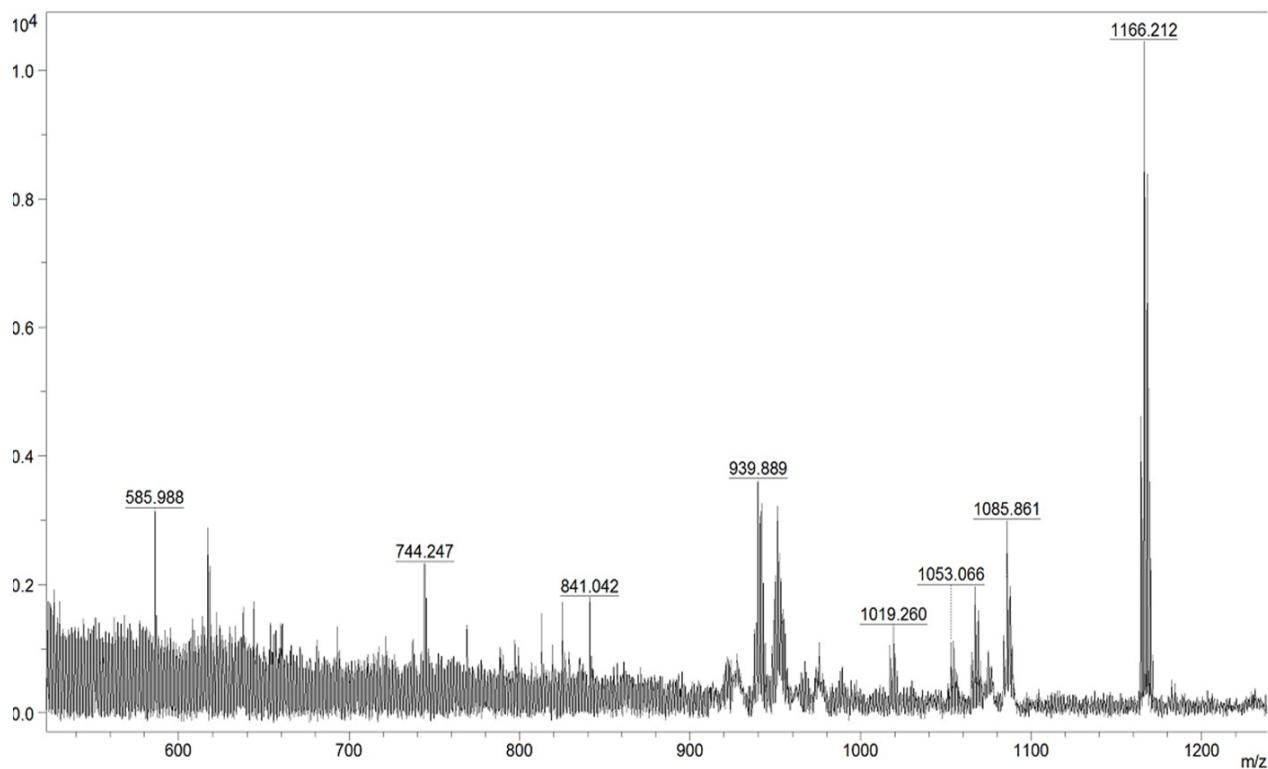


Figure S13-C ^{13}C NMR spectrum of BTZPZP



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Figure S-14 Maldi mass spectrometry for BTZPZP

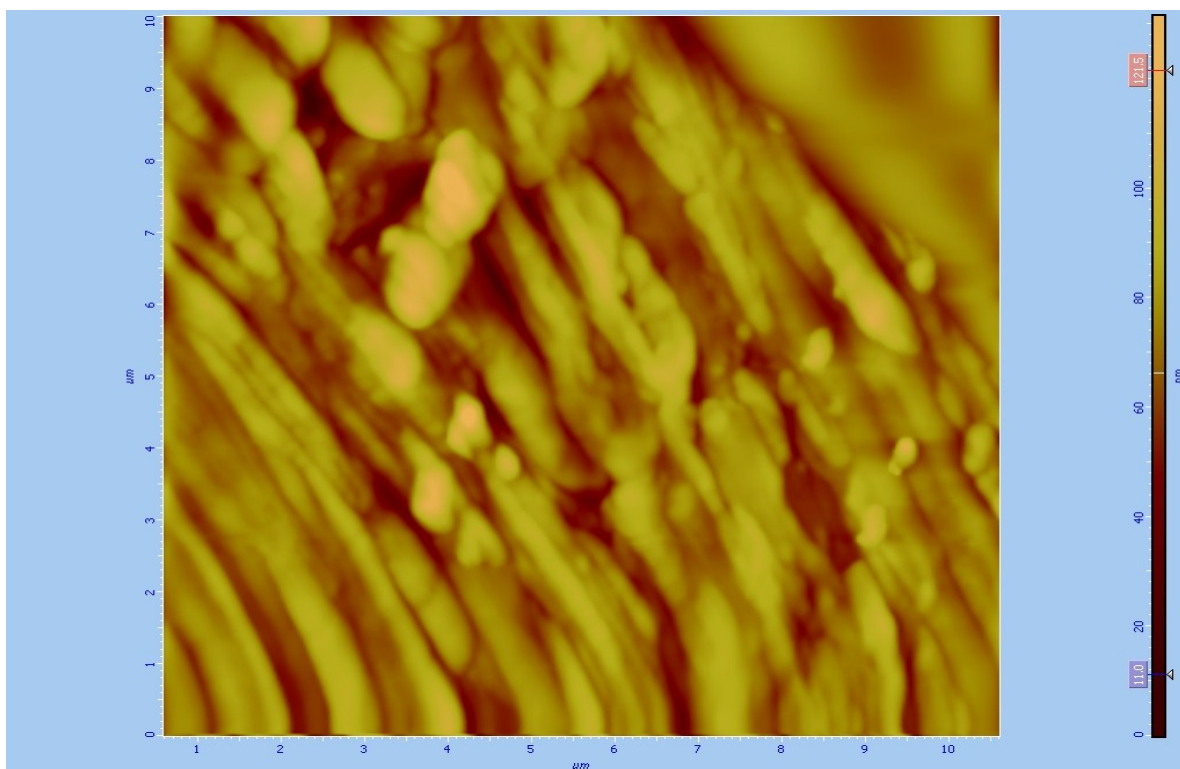


Figure S-15 AFM image for BTZPZP monomer.

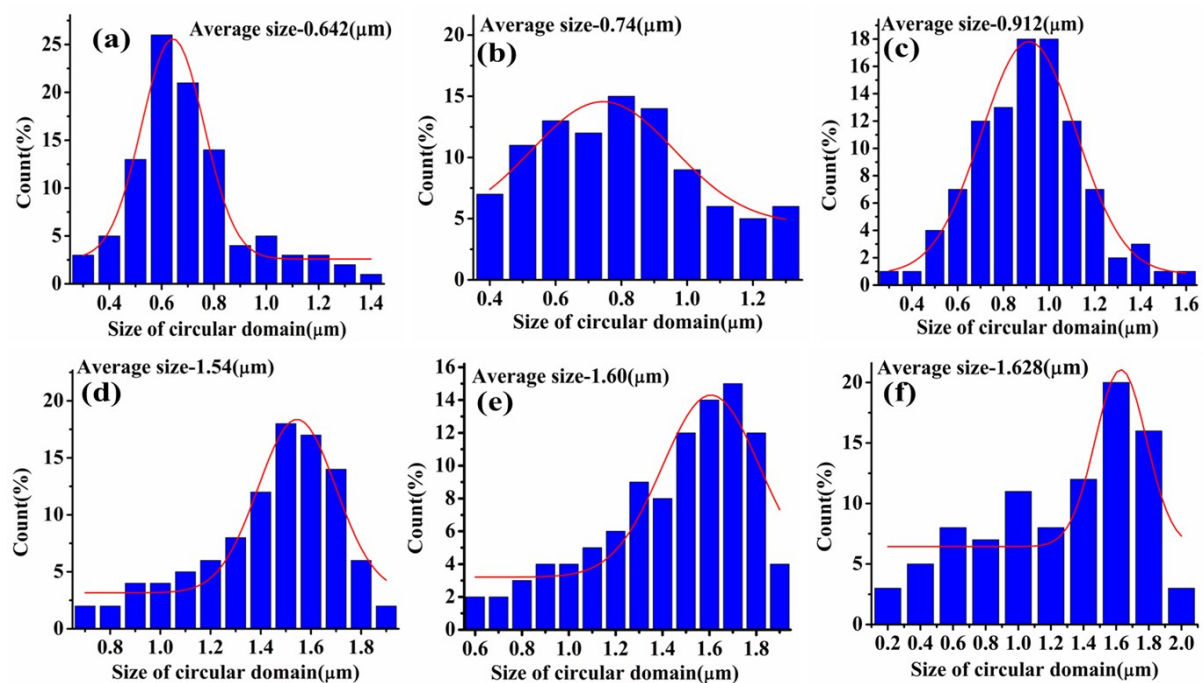


Figure S-16 Histogram of the height distribution of P-BTZPZP copolymers. a) P-BTZPZP-0.125, b) P-BTZPZP-0.25, C) P-BTZPZP-0.5, d) P-BTZPZP-1, e) P-BTZPZP-2.5 and f) P-BTZPZP-5.0.

Statistical analysis of P-BTZPZP copolymers from AFM images

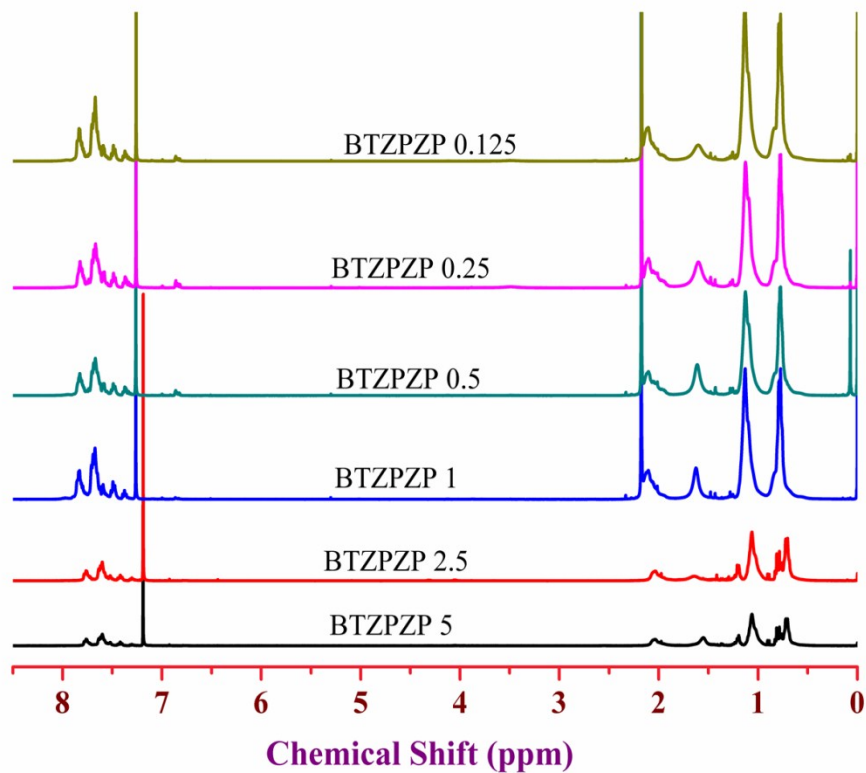


Figure 16: ^1H NMR Spectrum of P(BTZPZP)- COPOLYMERS

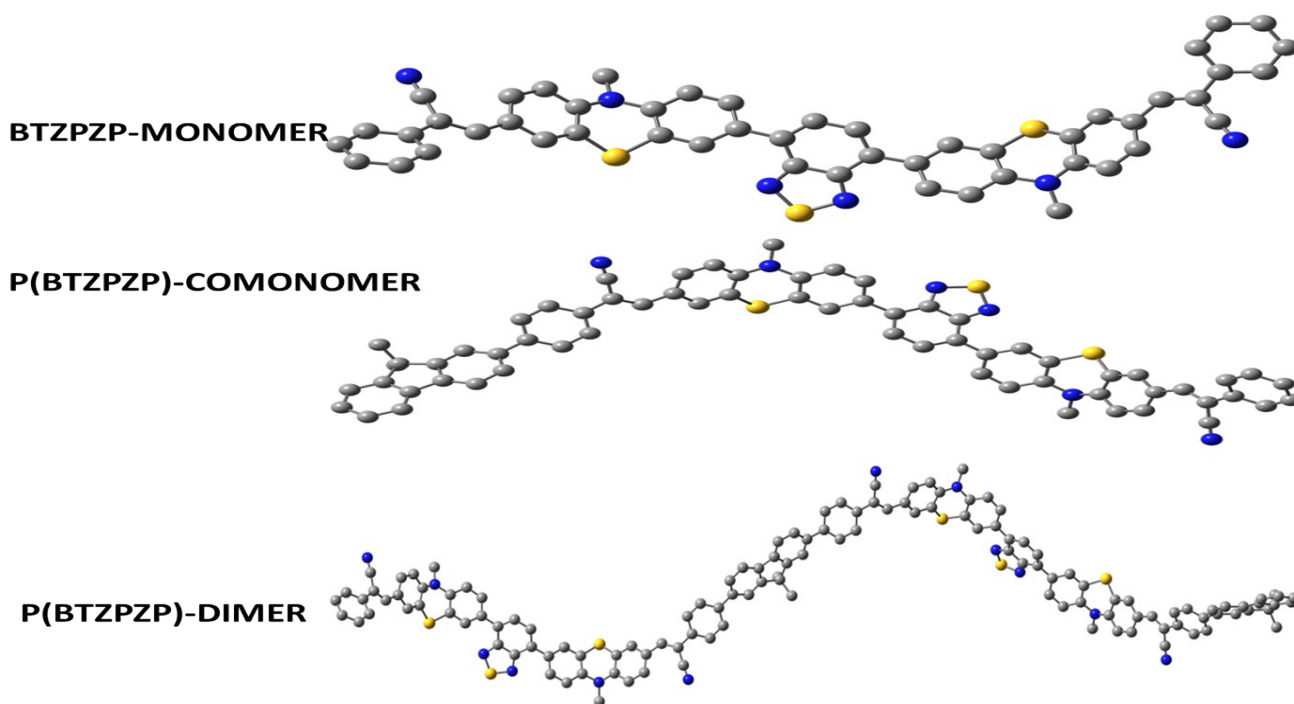


Figure 17: Optimized geometry at B3LYP/6-31G* level of theory. The Hydrogen atoms omitted here for clarity

Computational Details:

The ground and excited state geometries of the two systems were optimized by using density functional theory (DFT) based method with Becke's three-parameter functional and the Lee–Yang–Parr functional (B3LYP)¹⁻² functional with 6-31G* basis set. Frequency calculations were also executed at the same level of theory. The optimizations and the vibrational data confirmed that the structures were true minima on the potential energy surface because there were no imaginary frequencies. On basis of gas phase optimized ground and excited state geometries, the absorption and emission spectral properties in chloroform (CHCl₃) were calculated by time dependant density functional theory (TD-DFT) method with Polarizable Continuum Model (PCM) at B3LYP 6-31G* level. All calculations were performed using Gaussian 09 program package³.

Reference:

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