Supplementary Information (SI) for Polymer Chemistry.

Supplementary Information

Thiazolothiazole linked solid-state emissive linear and porous organic polymers utilizing tetraphenyl buta-1,3-diene AIE active building blocks

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S1. Experimental Procedures

S1.1. Materials

All the reagents were procured commercially and used without purification unless otherwise mentioned. Phenyl acetylene, 4-tertbutylphenyl acetylene, 4-bromobenzaldehyde, trimethylsilylacetylene, $CuBr_2$, $PdCl_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ were bought from Sigma Aldrich, $Pd(dppf)Cl_2$.DCM and rubeanic acid were purchased from TCI chemical and 4-formylphenyl boronic acid, 4-bromoanisole, bis(pinacolato)diboron were purchased from AVRA chemicals and NaOH, KOH, KOAc, K_2CO_3, anhydrous Na_2SO_4 were purchased from Merck India Pvt. ltd. The solvents used for the synthesis purpose were from Merck India Pvt. Ltd. and Avantor® (RANKEM). For spectroscopic measurement the HPLC grade solvents were used as solvent. For drying of THF for reaction purpose, Na metal was used as drying reagent. The column chromatography was performed on silica gel (100-200 mesh).

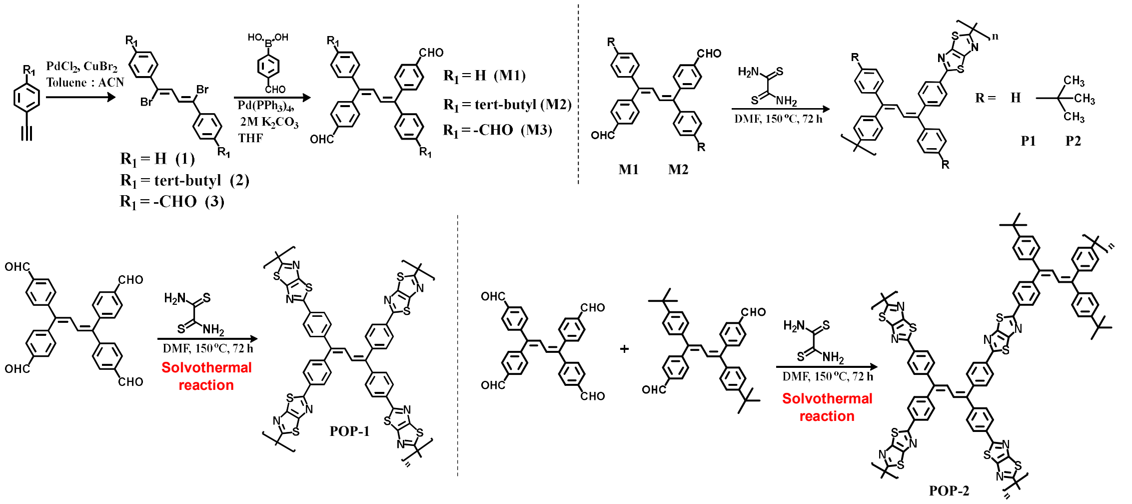
S1.2. Methods and instruments

NMR experiment was performed on 500 and 400 MHz Bruker DPX spectrometer using $CDCl_3$ and DMSO-D6 as solvent and TMS as standard reference at room temperature, with chemical shift given in parts per million (ppm). Matrix-assisted laser desorption ionization - time of flight (MALDI-TOF) mass spectrometry was done with Bruker Ultraflextreme (Bruker Daltonics Pvt. Ltd.) using diathranol (10 mg dissolved in 1 mL of THF) as a matrix and for sample preparation, 10µL of the sample solution (1 mg/mL in DCM) was added to 10 µL of matrix solution. FT-IR spectra were recorded in HORIBA FT - 720 FT-IR spectrometer using the pellets of the samples diluted with dry KBr. N_2 sorption measurements are carried out in 3Flex surface area analyzer by Micromeritics and pore size distribution was obtained using non-local density functional theory (NLDFT) method. Prior to the experiment the samples have passed through the solvent exchanged process with methanol and it has been kept in vacuum for 24 h at 100 °C. The dried samples have been further degassed with N_2 at 120 °C immediately prior to the measurement. Thermal gravimetric analysis (TGA) was done by PerkinElmar TGA 4000 thermogravimetric analyzer where heat flow was set to be 10 °C / min under controlled nitrogen flow. X-ray diffraction pattern of the powder of the polymers were performed in Bruker D-8 Advanced SWAX, Germany diffractometer using Ni-filtered Cu Kα (λ = 0.15406 nm). Field emission scanning electron microscopy (FE-SEM) experiment was performed in JEOL instrument (JSM-7500F). UV–vis absorptions spectra of the monomers and linear polymers and UV-Vis diffuse reflectance spectra (DRS) of the porous polymers were studied with Agilent carry-5000 spectrophotometer. Photoluminescence (PL) spectra and PL decay profile in Time correlated single photon counting (TCSPC) were obtained from FLS1000 steady-state and transient fluorescence spectrometer. For optical studies (PL, TCSPC and PLQY) in solution, 10^{-5} M solutions of the monomers and linear polymers in chloroform were used whereas for the insoluble porous polymers, the compounds were sonicated for 1 h in ethanol and the suspension solutions of ethanol were used. For the studies in solid state, drop-casted neat films of the compounds and/or powder samples were used. The absolute photoluminescence quantum yield (PLQY) measurements in solution as well as in solid state were carried out in the same instrument using integrated sphere. The temperature dependent PL measurements of all the compounds were performed in toluene due to its high boiling point. To study electrochemical properties of the monomers and linear polymers cyclic voltammetry (CV) experiment was performed in CHI6087E electrochemical workstation under nitrogen atmosphere at room temperature. Three electrodes used in CV were as follows: a glass carbon disk (Φ= 3 mm) used as the working electrode, a platinum wire as the standard electrode and Ag/Ag^+ as the reference electrode, which were standardized for the redox couple ferrocenium/ferrocene.

DFT calculation: Density functional theory (DFT) calculations were performed using Gaussian 16 suit of programs. All the required structures were optimized employing a hybrid DFT functional namely B3LYP and 6-31G(d) basis set. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were also calculated at the same level of theory and structures were visualized using Avogadro software and Mercury software.

S2. Results and discussion

S2.1. Synthesis and Characterization



Scheme S1. Synthesis scheme for all the monomers and polymers.

Synthesis procedures

Synthesis of the intermediate compounds (1, 2 and 3) were done by following the previously reported procedures.[1]

Synthesis of monomers: Compound 1(for M1)/ Compound 2 (for M2)/ compound 3 (for M3) (0.25 mmol), (4-formylphenyl) boronic acid (0.625 mmol), $Pd(PPh_3)_4$ (0.025 mmol) and K_2CO_3 (2M) were taken into a two-neck round bottomed flask. 15 mL anhydrous tetrahydrofuran was added to the flask under N_2 atmosphere and the mixture was stirred at 65 °C for 24 h. The reaction mixture was washed with brine solution, extracted in $CHCl_3$ and dried over anhydrous sodium sulphate (Na_2SO_4). The organic solvent was completely evaporated and the residue was purified by column chromatography using DCM/petroleum ether (1:2) as eluent. The product was further recrystallized by evaporating the solution of DCM and MeOH mixture.

M1: The product was obtained as greenish white crystals; amount: 78 mg, 0.188 mmol, yield: 75%. ^{1}H NMR (400 MHz, DMSO-D$_6$)): δ (ppm)= 10.08 (s, 2H), 8.04 (d, 4H), 7.56 (d, 4H), 7.33-7.27 (m, 6H), 7.10-7.15 (m, 4H), 6.69 (s, 2H). ^{13}CNMR (100 MHz, DMSO-D$_6$): δ (ppm) 193, 145, 144, 141, 136, 131, 130, 129, 128, 127, 126. MALDI-TOF: (m/z) calculated for $[M+H]^+$: 415.17, found: 415.02. FT-IR (cm^{-1}): 1698 (C=O stretching of -CHO).

M2: The product was obtained as yellowish white crystals; amount: 90 mg, 0.17 mmol, yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 10.08 (s, 2H), 7.94 (d, 4H), 7.49 (d, 4H), 7.28 (d, 4H), 7.04 (d, 4H), 6.74 (s, 2H), 1.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 191.96, 151.29, 146.51, 143.32, 138.4, 135.54, 131.41, 129.74, 127.29, 125.72, 125.39, 34.6, 31.23. MALDI-TOF: (m/z) calculated for $[M+H]^+$: 527.30, found: 527.03. FT-IR (cm^{-1}): 1701 (C=O stretching of -CHO).

M3: The product was obtained as yellow crystals; amount: 71 mg, 0.15 mmol, yield: 60% .^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 10.11 (s, 2H), 9.98 (s, 2H), 8.01 (d, 4H), 7.79 (d, 4H), 7.51 (d, 4H), 7.29 (d, 4H), 6.87 (s, 2H).

^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 191.72, 191.54, 146.88, 144.99, 144.46, 136.27, 135.94, 131.39, 130.16, 130.02, 128.37, 128.20. HRMS (m/z) calculated for $[M+H]^+$: 471.16, found: 471.11. FT-IR (cm^{-1}): 1690 (C=O stretching of -CHO).

Synthesis of linear polymers: The monomers M1 or M2 (0.25 mmol) and rubeanic acid (0.3 mmol) were taken into a 50 mL two-necked round bottom flask and degassed with nitrogen. 10 mL of anhydrous DMF was added and the solution was refluxed at 150 °C for 72 hr. After cooling to room temperature, the reaction mixture was added to excess amount of hexane to get dark yellow precipitate which was further washed with 30 mL MeOH for three times (vortex for 5 mins and then centrifuge) to remove the reactants and oligomers. The product was dried in vacuum oven and collected as brown solid.

Synthesis of porous polymers:

POP-1: Monomer M3 (0.12 mmol) was dissolved in 1 mL of anhydrous DMF and transferred to a Pyrex glass tube with syringe. Similarly, rubeanic acid (0.26 mmol) was also dissolved in 1 mL of anhydrous DMF and transferred to the same glass tube and the mixture was sonicated for 10 mins until completely dissolved. After three cycles of freeze, pump and thaw the glass tube was sealed under vacuum and kept inside a hot air oven at 150 °C for 72 h. The sealed glass tube was brought to room temperature and cut to open to collect the reaction mixture. The mixture was added into 20 mL of MeOH and the precipitate was collected. Further purification was done by Soxhlet extraction method using different solvents (MeOH, DCM and THF) for 12 h with each solvent.

POP-2: Monomer M3 (0.06 mmol) and M2 (0.06 mmol) was dissolved in 1 mL of anhydrous DMF were transferred to a Pyrex glass tube along with rubeanic acid (0.26 mmol) dissolved in 1 mL of anhydrous DMF with a syringe and the mixture was sonicated for 10 mins until completely dissolved. After three cycles of freeze, pump and thaw the glass tube was sealed under vacuum and kept inside a hot air oven at 150 °C for 72 h. The sealed glass tube was brought to room temperature and cut to open to collect the reaction mixture. The mixture was added into 20 mL of MeOH and the precipitate was collected. Further purification was done by Soxhlet extraction method using different solvents (MeOH, DCM and THF) for 12 h with each solvent.

Characterization of synthesized compounds

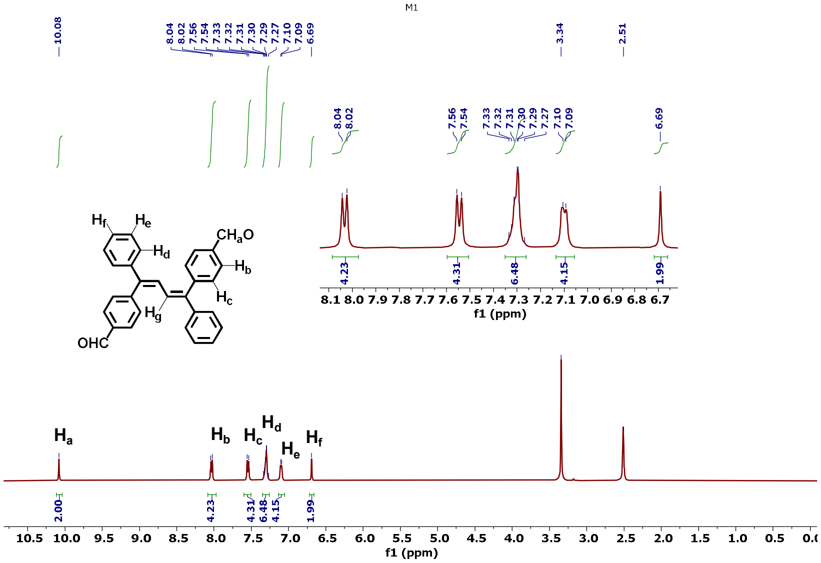


Fig. S1 ^{1}H NMR spectrum of M1 in DMSO-D6.

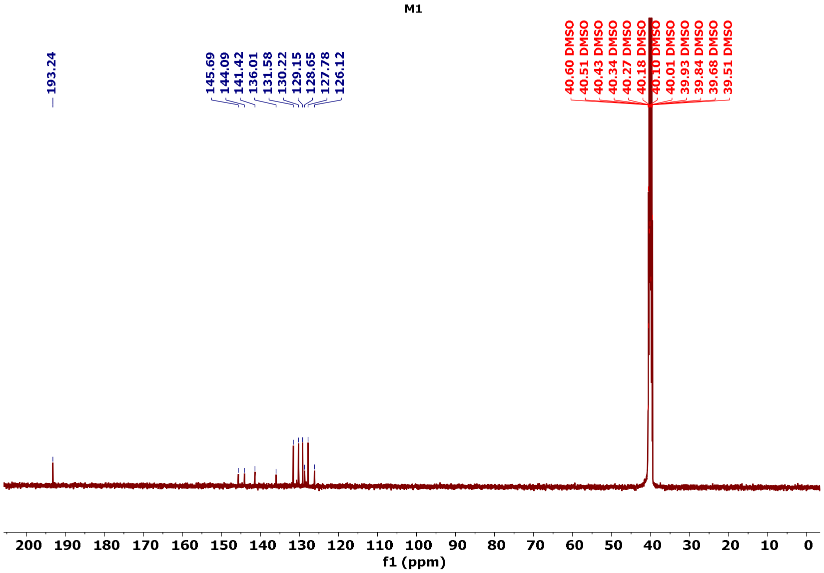


Fig. S2 ^{13}C NMR spectrum of M1 in DMSO-D6.

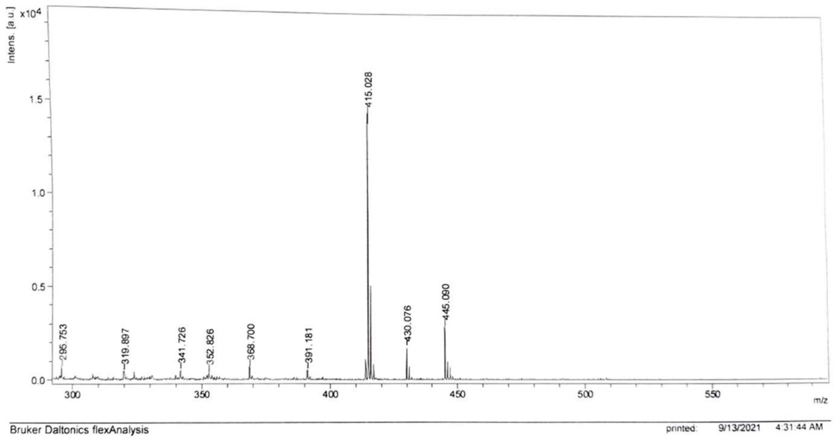


Fig. S3 MALDI-ToF data of M1.

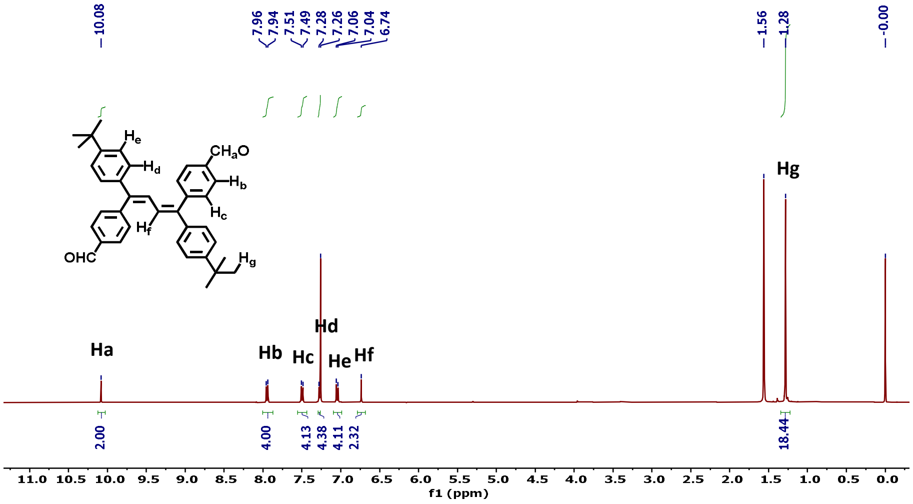


Fig.S4 ^{1}H NMR spectrum of M2 in $CDCl_3$.

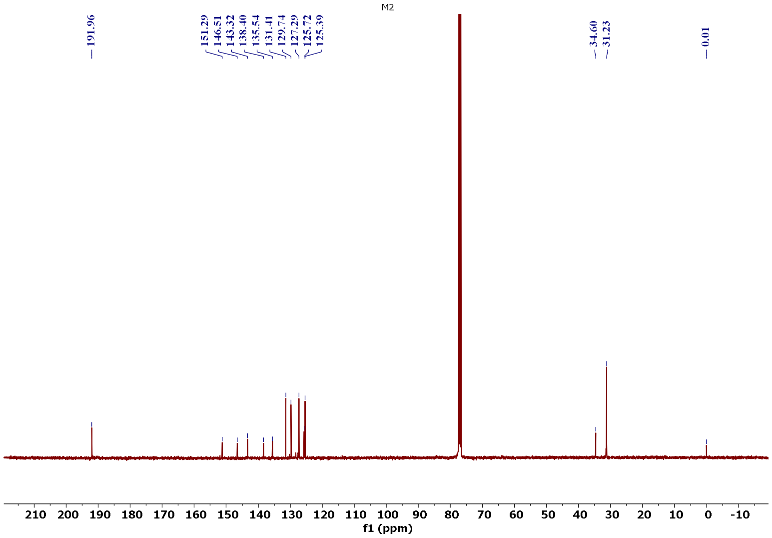


Fig. S5 ^{13}C NMR spectrum of M2 in $CDCl_3$.

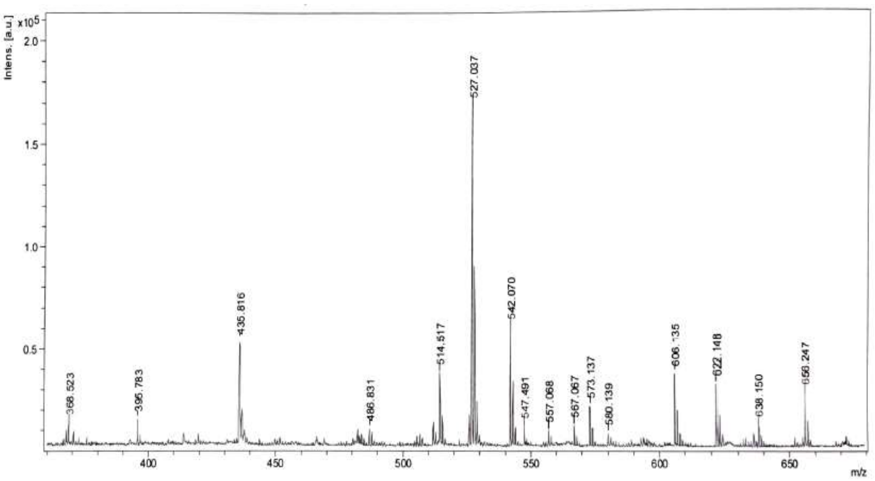


Fig.S6 MALDI-ToF data of M2.

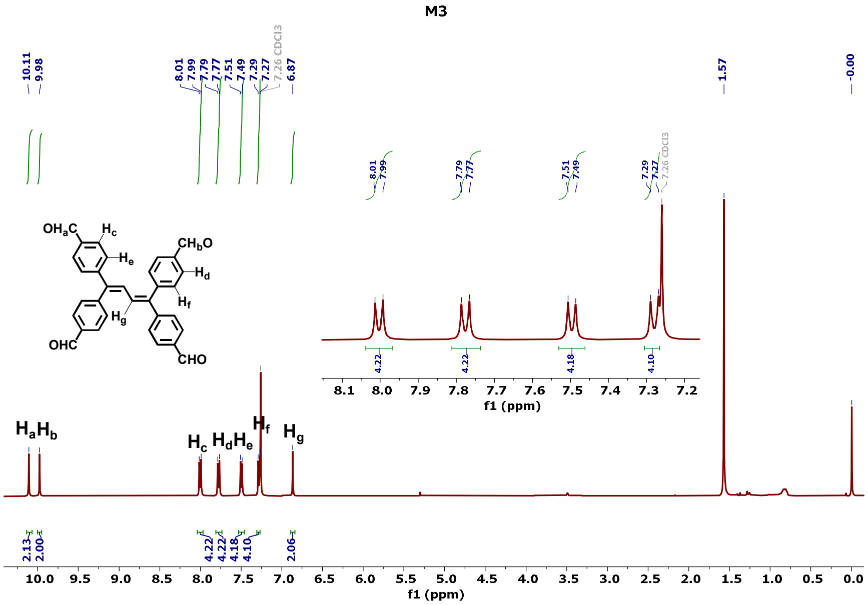


Fig. S7 ^{1}H NMR spectrum of M3 in $CDCl_3$.

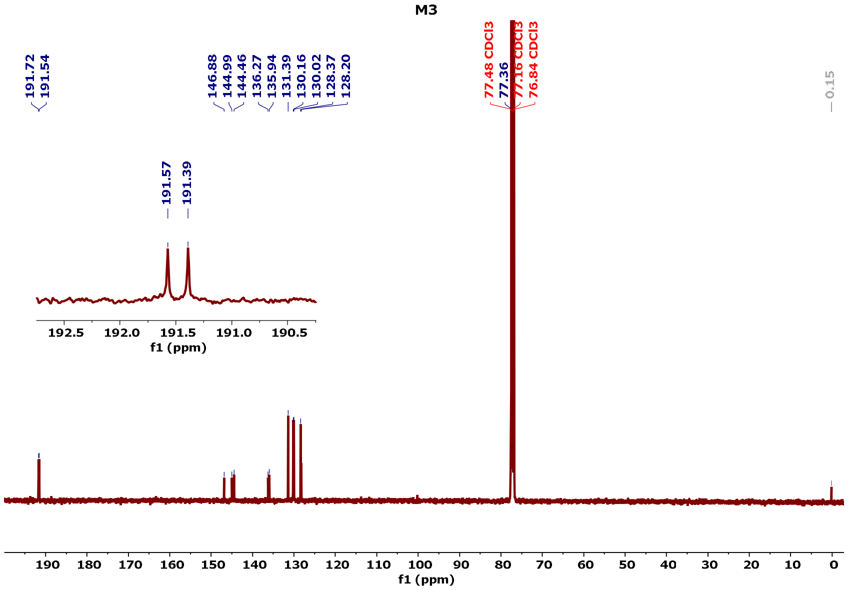


Fig.S8 ^{13}C NMR spectrum of M3 in $CDCl_3$.

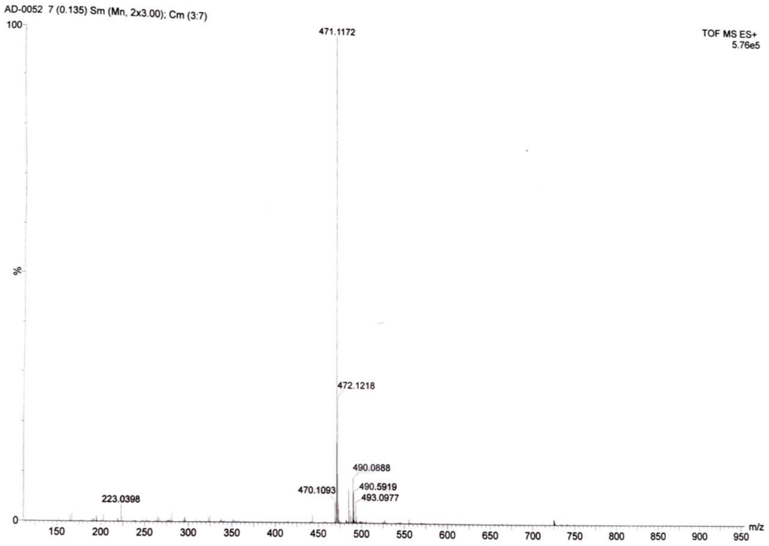


Fig.S9 HRMS data of M3.

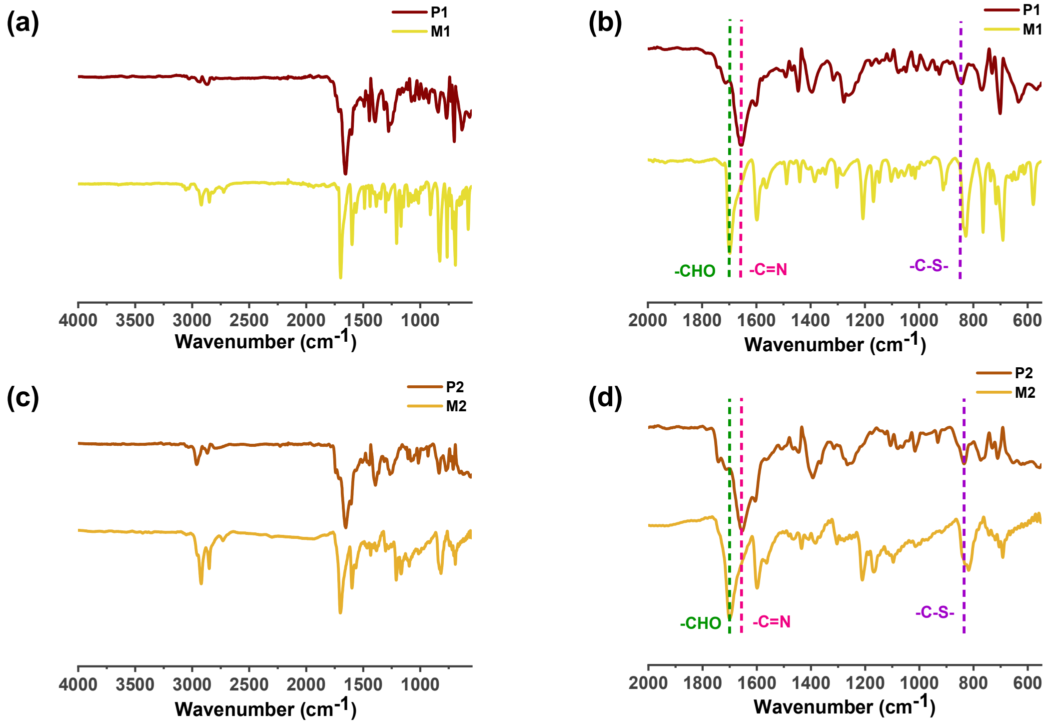


Fig. S10 FT-IR spectra of M1 and P1 (a and b) and M2 and P2 (c and d).

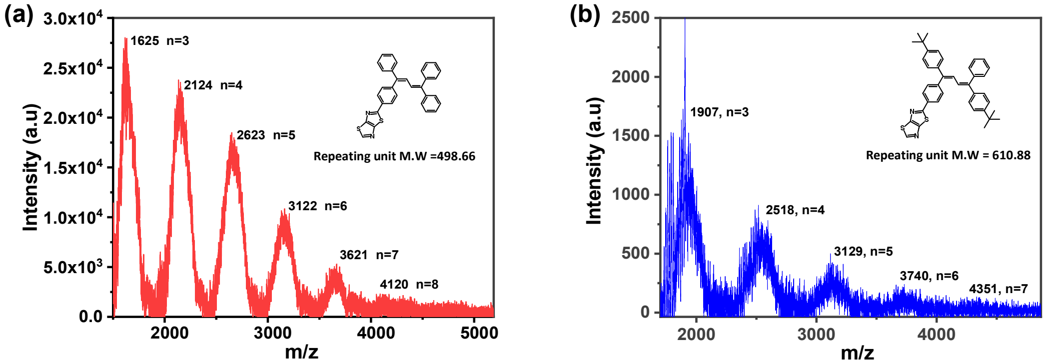


Fig. S11 MALDI-TOF data of P1 (a) and P2 (b).

S2.2. PXRD, N_2 adsorption-desorption and FESEM study

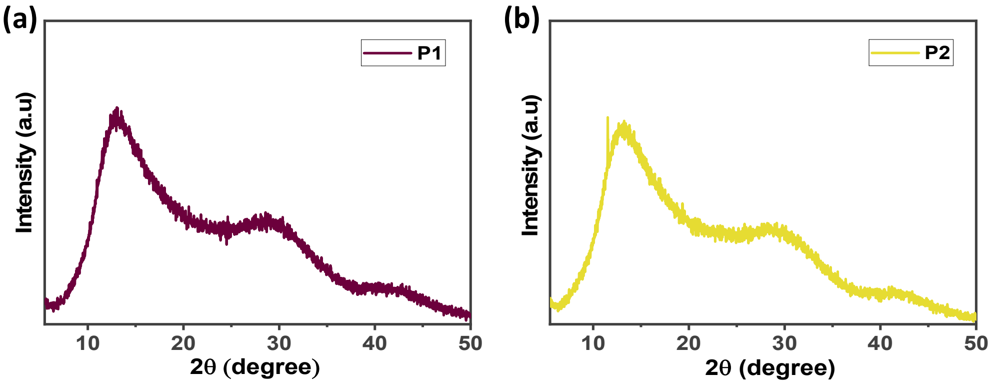


Fig. S12 Powder XRD data of P1 (a) and P2 (b).

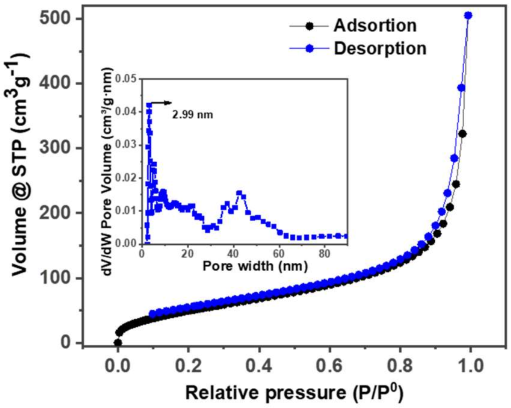


Fig. S13 N_2 adsorption and desorption data of POP-2 (inset: dV/dW pore volume versus pore width data of POP-2 obtained from NLDFT).

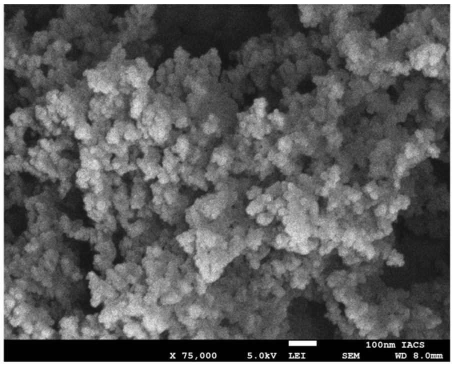


Fig. S14 SEM image of POP-2.

S2.3. DFT study

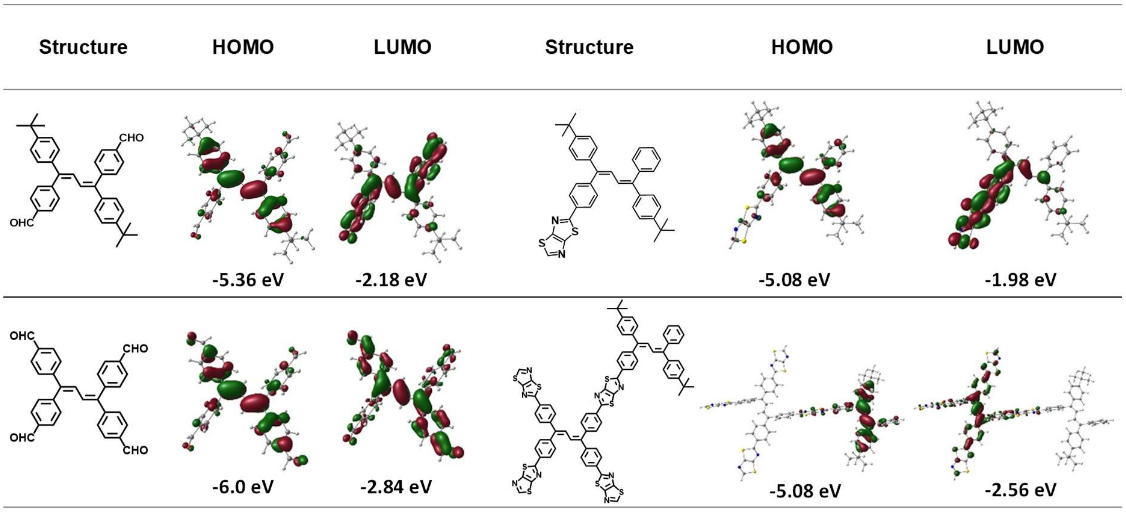


Fig. S15 Structures of HOMO and LUMO and their corresponding energies of the monomers M2 and M3 and repeating unit of P2 and POP-2.

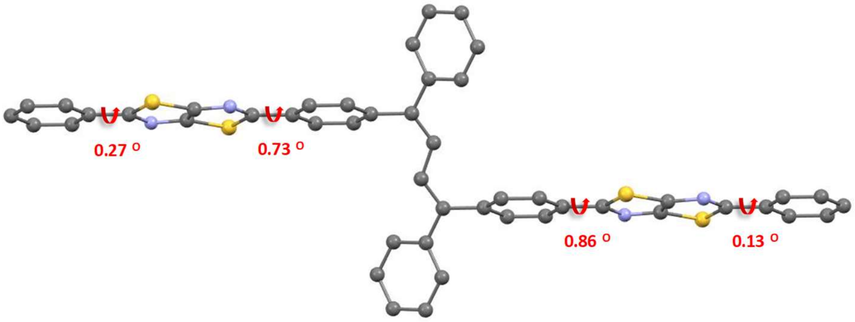


Fig. S16 Optimized structure of the extended repeating unit of P1 the twisting angles between the thiazolothiazole ring and the adjacent phenyl rings are shown.

S2.4. Thermal gravimetric study

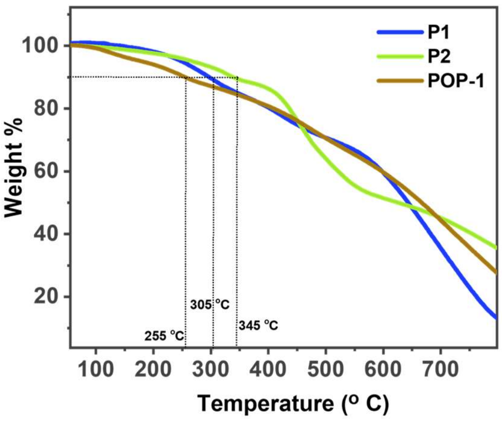


Fig. S17 TGA data of the polymers. Decomposition temperatures corresponding to 10% weight loss are mentioned for each polymer.

S.2.5. Photophysical studies

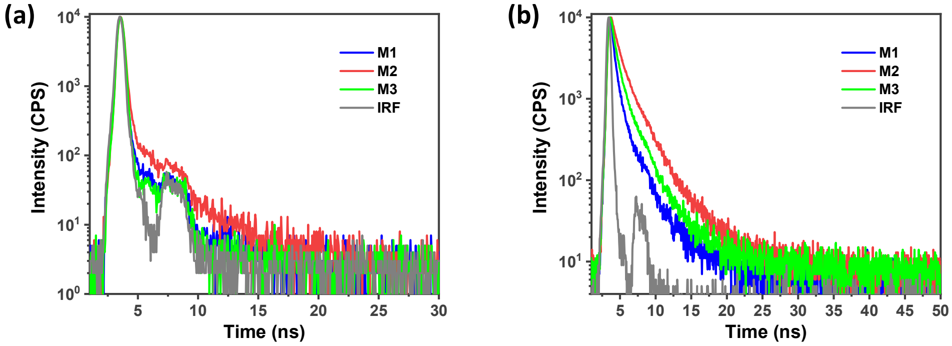


Fig. S18 a) PL decay profile of monomers in DCM and b) PL decay profile of monomers in film state. (In solution the lifetime values of the monomers are very less which are almost close to IRF therefore the lifetime measurements are not very accurate.)

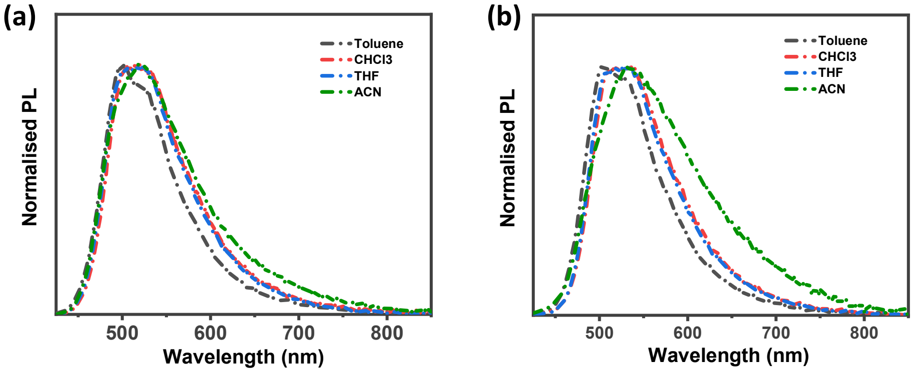


Fig. S19 PL spectra of a) P1 and b) P2 in different solvent polarity.

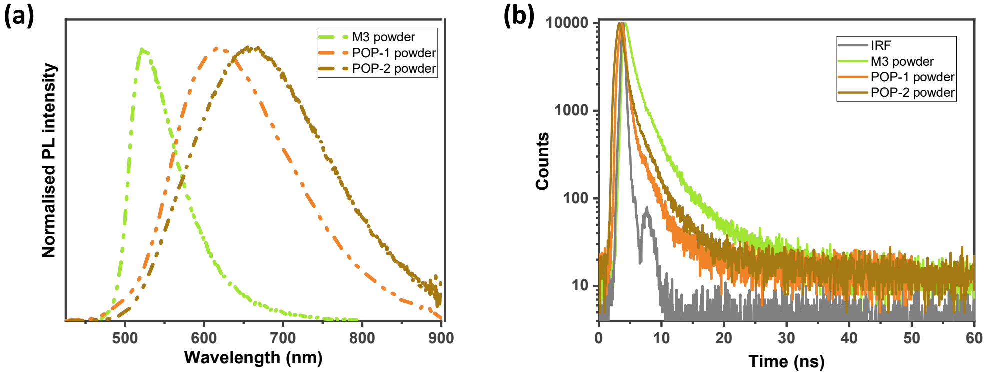
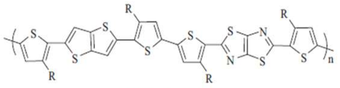
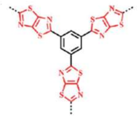
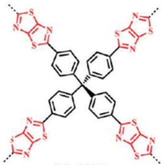
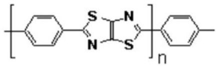
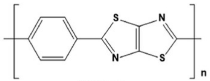
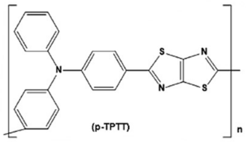
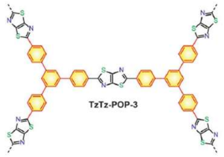
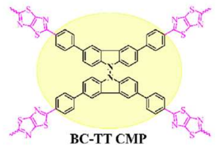
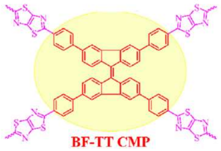
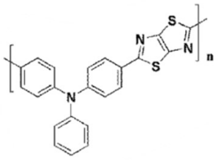
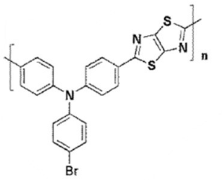
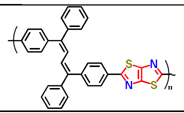
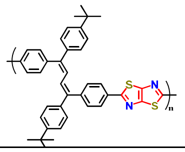
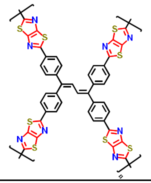
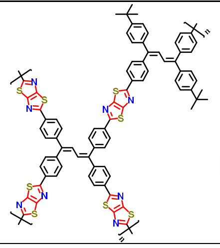


Fig. S20. a) PL of vacuum dried powders of M3, POP-1 and POP-2 and b) their PL decay profile.

Table S1: **Literature survey on thiazolothiazole based emissive polymers and their absorption / emission maxima and PLQY values in solution and solid state.**

Polymer structure		**Absorption maxima (nm) Solution/ solid**	**Emission maxima (nm) Solution/ solid**	**PLQY (%) Solution/ solid**	**Reference**
 PTT-Tz-C12 (R = $C_{12}H_{25}$) PTT-Tz-C14 (R = $C_{14}H_{29}$) PTT-Tz-C16 (R = $C_{16}H_{33}$)	C12	571, 618/ 564, 614	589, 635/ 678	*Not reported*	***2***
	C14	578, 624/ 569, 618	589, 632/ 674	*Not reported*	
	C16	577, 625/ 568, 616	588, 632/ 671	*Not reported*	
 TzTz-POP-1		*Not reported*	*Not reported*	*Not reported*	***3***
 TzTz-POP-2		*Not reported*	*Not reported*	*Not reported*	
 p-PhTT		380,420/ -	467,497/ -	*Not reported*	***4***
 (p-PhTT)		264/ 490	459/ -	*Not reported*	***5***
 (p-TPTT)		444,555/-	520/ -	*Not reported*	***6***
 TzTz-POP-3		400/ -	525/ -	*Not reported*	***7***
 TzTz-POP-4		422/ -	550/ -	*Not reported*	
 TzTz-POP-5		414/ -	575/ -	*Not reported*	

 BC-TT CMP	-/ 460	-/ 480	*Not reported*	***8***
 BIPE-TT CMP	-/ 276	-/ 435	*Not reported*	
 BF-TT CMP	-/ 272	-/ 425	*Not reported*	
 **P2**	434/ 320	520 / 517	*Not reported*	***9***
 **P4**	426 / 431	521 / 516	*Not reported*	
 **P1**	**404/ 417**	**516/ 675**	**28.4 / 3.6**	**Current work**
 **P2**	**404/ 428**	**528/ 632**	**35 / 9.3**	
 **POP-1**	**-/ 400**	**570/ 565**	**11 / 17.7**	
 **POP-2**	-/ -	**571/ 565**	**7.8 / 11.4**	

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