Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis and Thermal Behaviour of Thiophene-Based Oxazine-Ring Substituted Benzoxazine Monomers & Polymers

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TOTAL: 16 Pages, 19 Figures and 3 Tables.

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General Experimental Information:

Materials. 2-Hydroxybenzophenone (99%), titanium (IV) chloride solution (1.0 M in dichloromethane), and sodium borohydride (ReagentPlus®, 99%) were purchased from Sigma-Aldrich; 2-thiophenemethylamine (ta, >98.0%(GC)(T)) from TCI chemicals; ammonium hydroxide (aq., 28% NH_3) from Alfa Aesar; methanol, toluene, dichloromethane, and sodium sulfate (anhydrous, 99%) from Rankem; paraformaldehyde from Fisher scientific whereas trichloroacetic acid (> 99%, puriss grade) was procured from Spectrochem. All solvents used were AR grade and used as received.

Characterization. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR), ^{13}C Distortionless Enhancement by Polarization Transfer (DEPT), 2D NMR, viz., ^{1}H−^{1}H COSY (Correlation Spectroscopy), ^{1}H−^{1}H NOESY (nuclear overhauser effect spectroscopy), ^{1}H−^{13}C HSQC (heteronuclear single quantum correlation), and HMBC (heteronuclear multiple bond correlation) experiments were recorded on a Bruker 400 MHz FT-NMR spectrometer using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane or any residual solvent as an internal standard to assist the assignment of signals for the structural elucidation of monomers. NMR acquisition and processing software was Bruker Topspin 3.5pl7 or MestReNova. Chemical shifts (δ) are reported in ppm, and multiplicity of signals are denoted s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet). Mass spectrometry analyses were carried out using Agilent HRMS Q-ToF 6540 Series equipped with electrospray ionization (ESI) mode. Crystallization methodologies adopted are mentioned in the syntheses section. Crystal structure of monomer is determined by measuring X-ray diffraction data on D8 Venture Bruker AXS single-crystal X-ray diffractometer equipped with CMOS PHOTON 100 detector having monochromatized microfocus sources (MoK_α = 0.71073 Å). Crystal data were collected at room temperature. The crystal structure was solved using the SHELX program implemented in APEX 3.36-38. The non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions and refined using a riding model with appropriate HFIX commands. Quantum chemical calculations were carried out using density functional theory (DFT) in GAUSSIAN 09 D.01.[1] The monomer structure was optimized using B3LYP/6-311++G (d,p) level of theory.[2] Molecular visualization was performed with ChemCraft 1.8 b595b software.[3] The polymerization behavior of monomers was evaluated using dynamic differential scanning calorimetry, DSC-3, Star system, Mettler Toledo. For DSC scans, samples (1 ± 0.5 mg) were enclosed in hermetic aluminum pans and heated from 30 to 300 °C at 10 °C/min under a constant flow rate of nitrogen at 50 mL/min. Prior to the experiments, the instrument was calibrated for temperature and enthalpy using standard indium and zinc. Thermal equilibrium was regained within 1-2 min (s) of sample insertion, and the exothermic reaction was considered completed when the recorder signal leveled off to the baseline. DSC kinetic study was performed to determine the E_a (activation energy) of the monomer toward polymerization. Thermogravimetric analysis (TGA) of polymer and monomer was performed using a Mettler Toledo thermogravimetric analyzer (TGA) with a built-in gas controller (TGA2 SF/1100) and fitted with an XP1U TGA balance (ultra-micro balance) under a 50 mL/min flow rate of nitrogen atmosphere in the temperature range of 35−800 °C at a heating rate of 10

°C/min. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS20 mid-infrared FTIR spectrometer equipped with an interferometer with KBr/Ge coated beam splitter and dynamic alignment and thermoelectrically cooled (TEC) DTGS detector and attenuated total reflectance diamond (iD5-ATR) accessory. Spectra were recorded in the range 4000-400 cm^{-1} with a resolution of 0.25 cm^{-1} and 32 scans were co-added to each spectrum. Raman spectroscopy was performed by using a see through micro-Raman spectrometer (STR) equipped with a 532 nm argon-ion laser source with a power of 2.5 mW and 50 X magnification objective lens.

Protocol for the synthesis of the compounds:

Synthesis of 3-(thiophen-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine (abbreviated as **PH-ta**):

An oven-dried 25 mL two-necked RB flask was charged with a magnetic stirring bar, 2-thiophenemethylamine (0.98 mL, 19.12 mmol), formaldehyde (0.96 g, 32 mmol), and phenol (1.2g, 12.76 mmol). The resultant mixture was stirred in an oil bath at 70 °C for 18 h. After cooling to room temperature, ethyl acetate was added to the reaction mixture, then washed with NaOH aqueous solution (3 N, 20 mL) followed by HCl aqueous solution (3 N, 20 mL), and then washed for additional three times with 30 mL of water and extracted in ethyl acetate (5 × 20 mL). The organic phase was combined and dried over sodium sulfate, filtered, and concentrated in vacuo to afford the pure white solid (1.68 g, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 5.0, 1.3 Hz, 1H), 7.15 (td, *J* = 8.2, 1.8 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.91 (s, 2H), 4.13 (d, *J* = 0.6 Hz, 2H), 4.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.16, 142.20, 127.93, 127.84, 126.73, 126.42, 125.53, 120.90, 119.92, 116.62, 81.96, 77.16, 50.60, 49.55; HRMS $(M+H)^+$ calcd. for $C_{13}H_{13}NOS$, 232.0791; found, 232.0784.

Synthesis of *2-(((thiophen-2-ylmethyl)amino)methyl)phenol* (**thiophenylaminophenol**):

To an oven-dried 25 mL two-necked RB flask charged with a magnetic stirring bar, salicylaldehyde (1.21 mL, 11.55 mmol), trichloroacetic acid (1.56 g, 11.5 mmol), and dry dichloromethane (10 mL) were added and stirred. The mixture was cooled to 0 °C and 2-thiophenemethylamine (1.41 mL, 13.78 mmol) was added. The resulting mixture was stirred for 4 h at room temperature under nitrogen. The reaction was quenched with a methanolic solution of sodium borohydride (2 mL of 6.5 M solution, 13.8 mmol) and stirred for an additional 2 h at room temperature. The mixture was made basic (pH ∼10, tested using pH-paper) with a 3 M aqueous solution of NaOH and extracted in dichloromethane (100 mL). The organic layer was separated, washed with water (2 × 50 mL) and brine (50 mL), and concentrated under reduced pressure. The crude product was dissolved in ether, acidified (pH ∼2, tested using pH-paper) with conc. HCl and extracted with water. The water extract was made basic (pH ∼11, tested using pH-paper) with aqueous ammonia (28% v/v) and extracted in ether, washed with water (5 × 50 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to give a yellow-colored liquid (2.01 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.19 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.97 (t, *J* = 2.4 Hz, 1H), 6.96 – 6.93 (m, 2H), 6.86 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.78 (td, *J* = 7.4, 1.1 Hz, 1H),

4.01 (d, J = 2.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.20, 147.43, 141.41, 129.01, 128.76, 127.06, 126.93, 126.26, 125.24, 124.13, 123.80, 122.13, 119.31, 116.59, 77.16, 51.49, 46.68; HRMS $(M+H)^+$ calcd. for $C_{12}H_{13}NOS$, 220.0791; found, 220.0816.

Synthesis of *2-phenyl-3-(thiophen-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine* (abbreviated as **PH-ta-*[2]*ph**):

Benzaldehyde (0.48 mL, 4.79 mmol), trichloroacetic acid (0.11 g, 0.68 mmol), and toluene (5 mL) were added to an oven-dried 25 mL two-necked RB flask charged with a magnetic stirring bar. The resultant mixture was stirred for 20 mins and then thiophenylaminophenol (1.5 g, 6.84 mmol) was added to it. The reaction mixture was stirred at RT for 8 h. The reaction mixture evaporated to dryness to remove toluene. Ethyl acetate (10 mL) was added to the reaction mixture, then washed with 3 N NaOH aqueous solution (5 × 20 mL), followed by of 1 N HCl aqueous solution (5 × 20 mL), and then washed for additional four times with 50 mL of water and extracted in ethyl acetate (3 × 20 mL). The organic phase was combined and dried over sodium sulfate, filtered, and evaporated to dryness to recover pale-yellow solid (1.71g, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.27 (d, J = 7.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.90 (dd, J = 5.0, 3.5 Hz, 1H), 6.85 (dd, J = 6.3, 1.0 Hz, 3H), 5.97 (s, 1H), 4.02 (d, J = 14.4 Hz, 1H), 3.95 (d, J = 14.5 Hz, 1H), 3.88 (d, J = 2.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.57, 143.38, 138.95, 128.56, 128.15, 128.02, 127.87, 126.70, 125.72, 125.21, 120.85, 119.77, 116.71, 89.86, 77.48, 77.16, 76.84, 48.94, 47.04; HRMS $(M+H)^+$ calcd. for $C_{19}H_{17}NOS$, 308.1106; found, 308.1104.

Synthesis of *2,4-diphenyl-3-(thiophen-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine* (abbreviated as **PH-ta-*[2,4]*ph**):

A clean oven-dried 50 mL two-necked RB flask was charged with a magnetic stirring bar, 2-thiophenemethylamine (1.23 mL, 11.92 mmol), benzaldehyde (1.65 mL, 16.2 mmol), and phenol (1.0g, 10.73 mmol). The resultant mixture was stirred in an oil bath at 75 °C for 48 h. After cooling to room temperature, 5% ethyl acetate in hexane solvent (20 mL) was added to the reaction mixture, then, washed with 40 mL of 3 N HCl aqueous solution followed by additional three times with 50 mL of water, and then it was made basic (pH ~9) with 3 N NaOH aqueous solution and re-extracted in 5% ethyl acetate in hexane. The organic phase was dried over sodium sulfate, filtered, and evaporated under a vacuum to obtain a yellow solid compound. The crude product was recrystallized in 2% ethyl acetate in hexane to afford pale yellow crystals (2.69 g, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.27 (m, 5H), 7.23 – 7.16 (m, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 7.1 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.82 (s, 1H), 5.79 (s, 1H), 5.06 (s, 1H), 3.92 (d, J = 14.6 Hz, 1H), 3.70 (d, J = 14.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.69, 143.47, 143.45, 137.97, 130.81, 129.20, 128.61, 128.37, 128.25, 128.11, 127.33, 126.62, 126.47, 126.09, 125.28, 120.74, 119.70, 117.24, 85.14, 77.16, 60.15, 45.19; HRMS $(M+H)^+$ calcd. for $C_{25}H_{21}NOS$, 384.1417; found, 384.1415.

1D NMR Spectra:

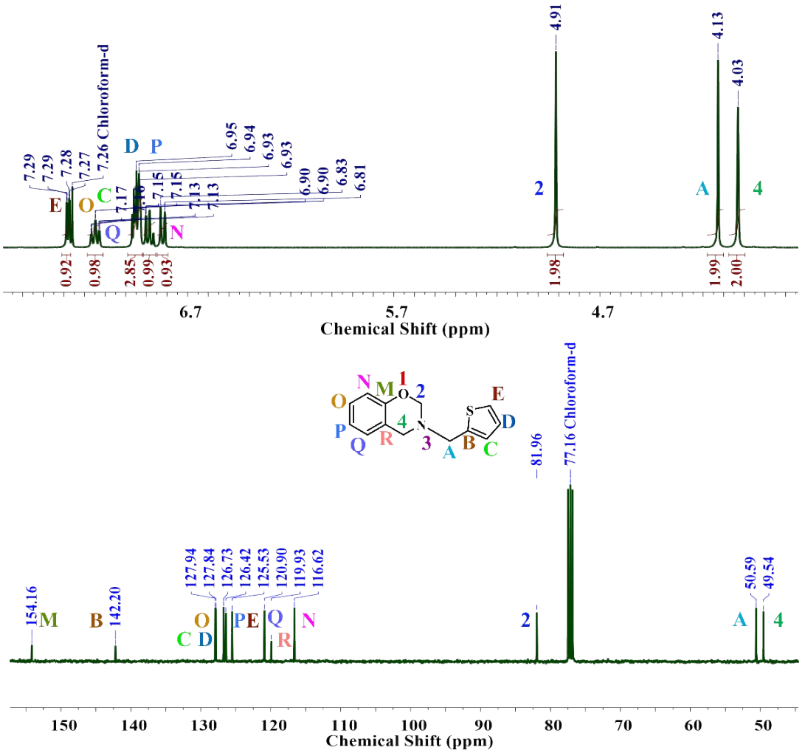
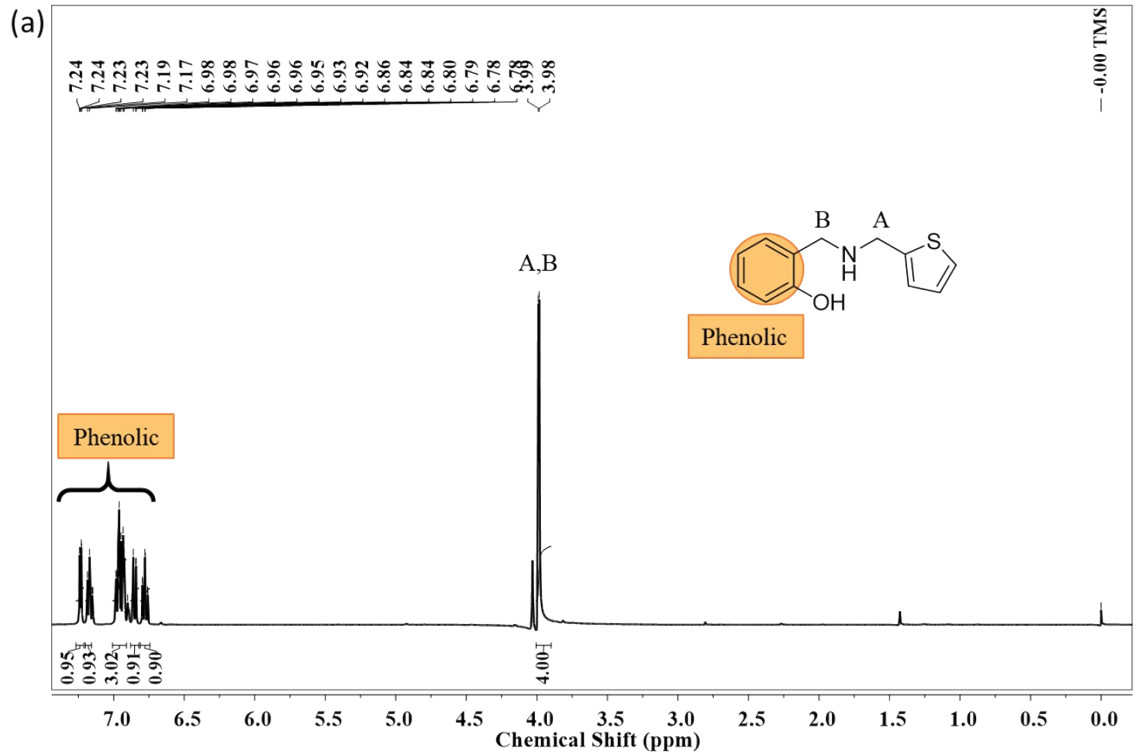


Figure S1. ^{1}H and ^{13}C NMR spectra of PH-ta.



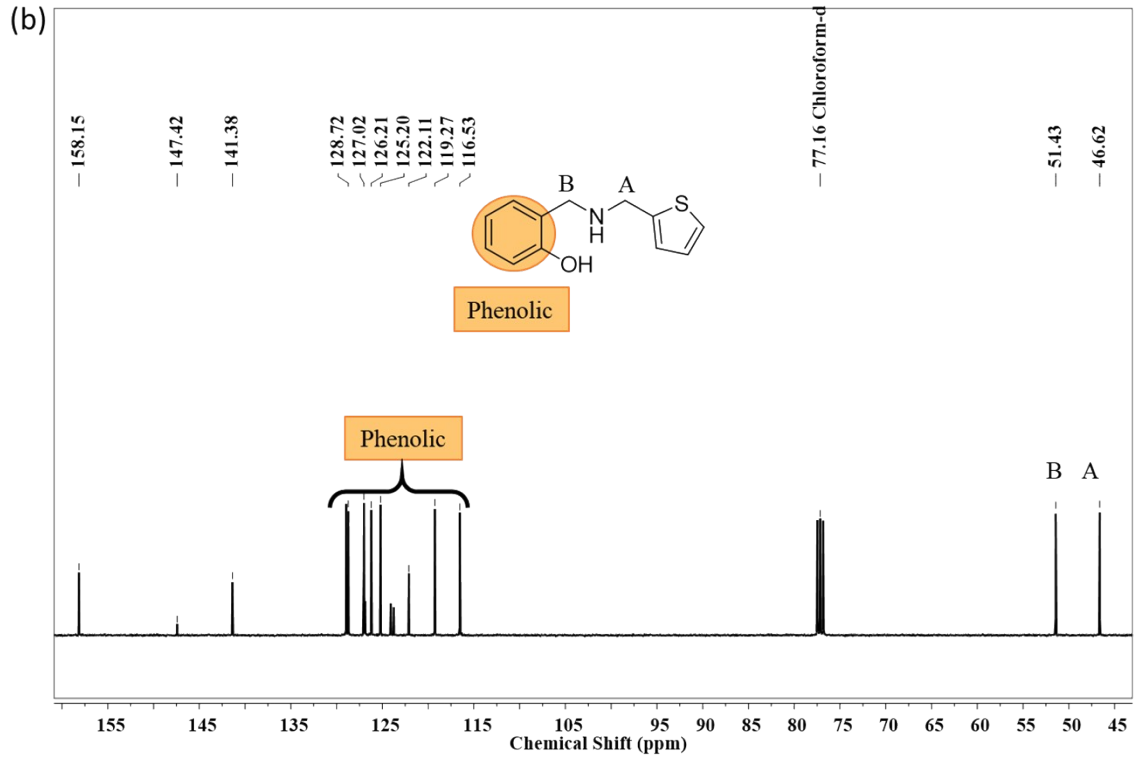


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of 2-hydroxy-*N*-thiophenylmethylamine [abbreviated as (thiophenyl)aminophenol].

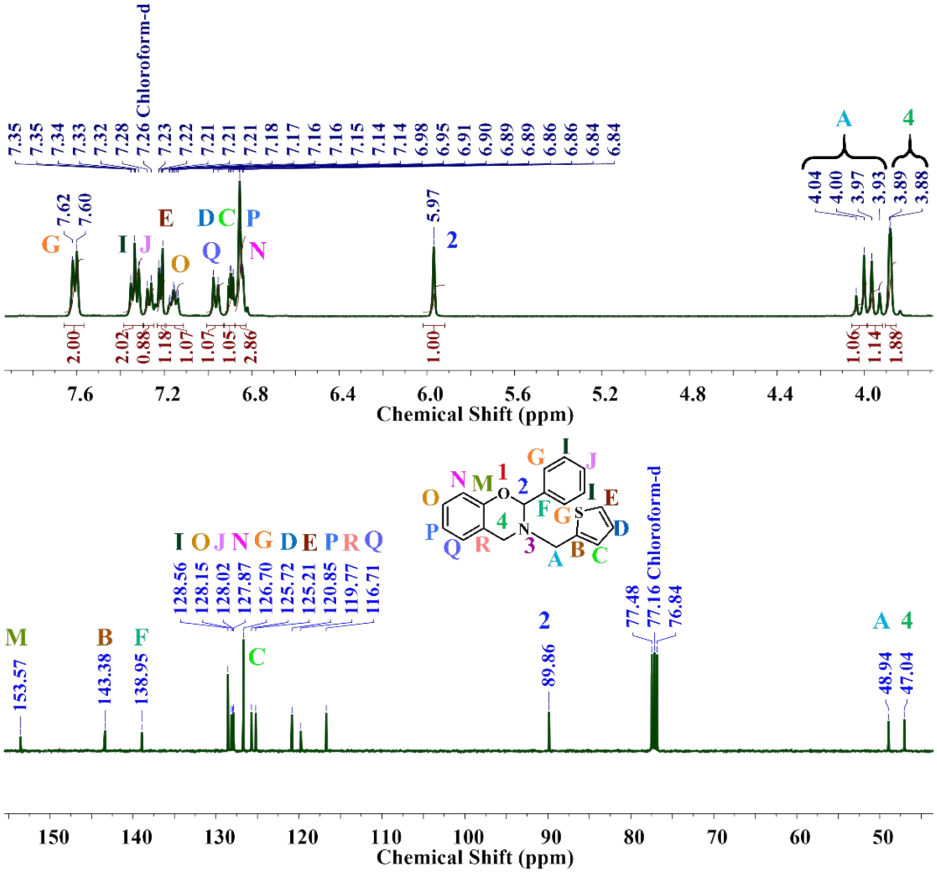


Figure S3. ^{1}H and ^{13}C NMR spectra of PH-ta-[*2*]ph.

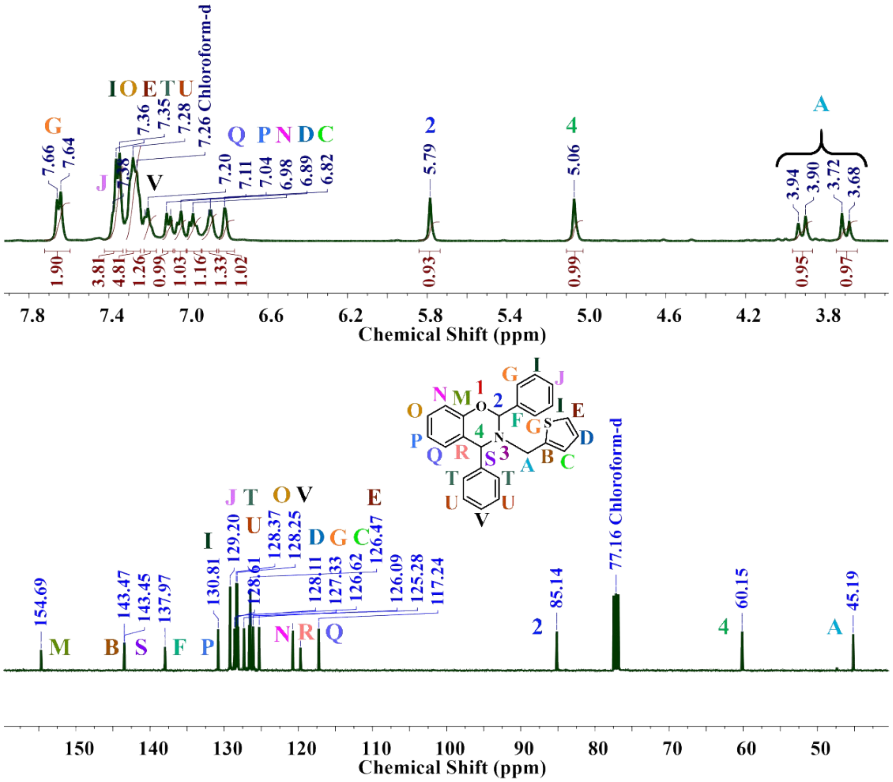


Figure S4. ^{1}H and ^{13}C NMR spectra of PH-ta-[*2,4*]ph.

2D NMR Spectra:

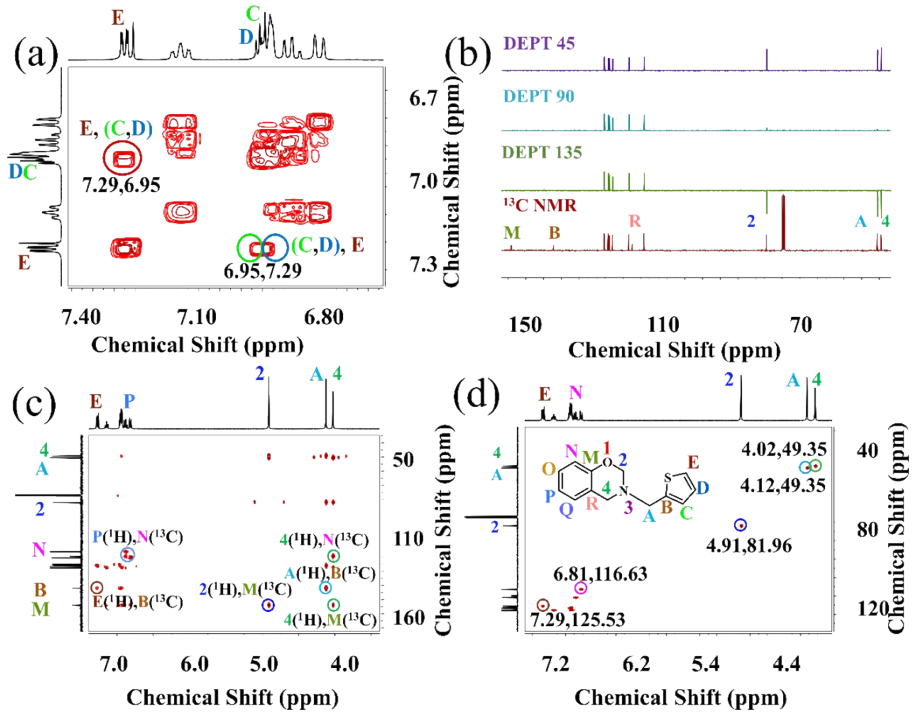


Figure S5. NMR spectra of PH-ta: (a) 2D $^{1}H–^{1}H$ COSY; (b) Stacked ^{13}C and DEPT 45/90/135; (c) 2D $^{1}H–^{13}C$ HMBC; (d) 2D $^{1}H–^{13}C$ HSQC.

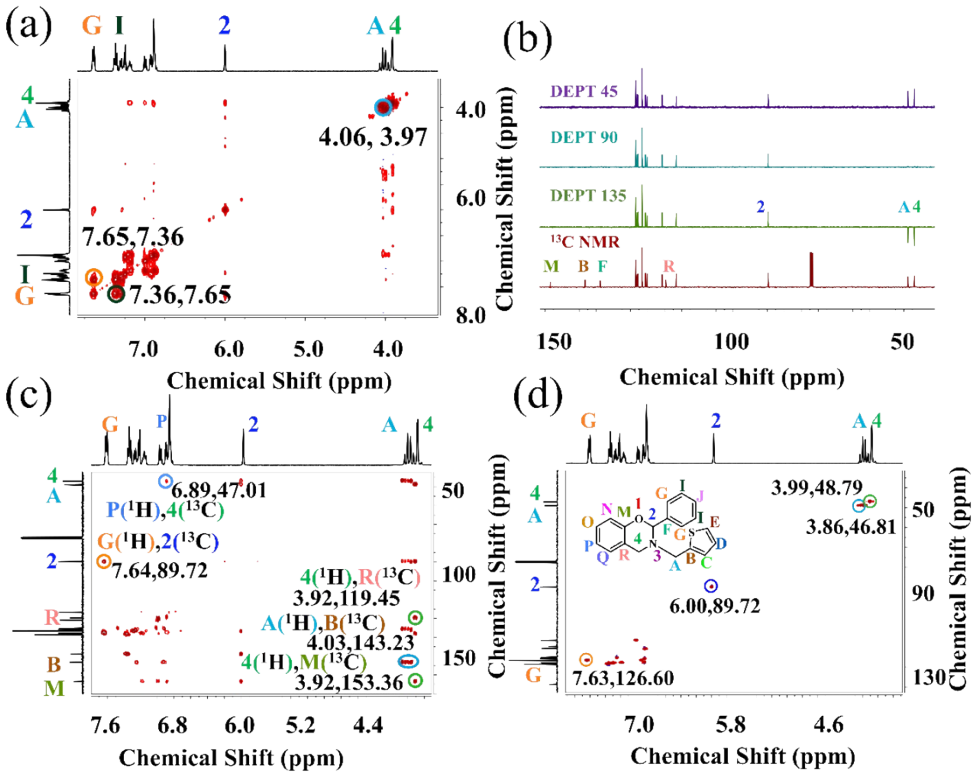


Figure S6. NMR spectra of PH-ta-[*2*]ph: (a) 2D ^{1}H–^{1}H COSY; (b) Stacked ^{13}C and DEPT 45/90/135; (c) 2D ^{1}H–^{13}C HMBC; (d) 2D ^{1}H–^{13}C HSQC.

HRMS of the compounds:

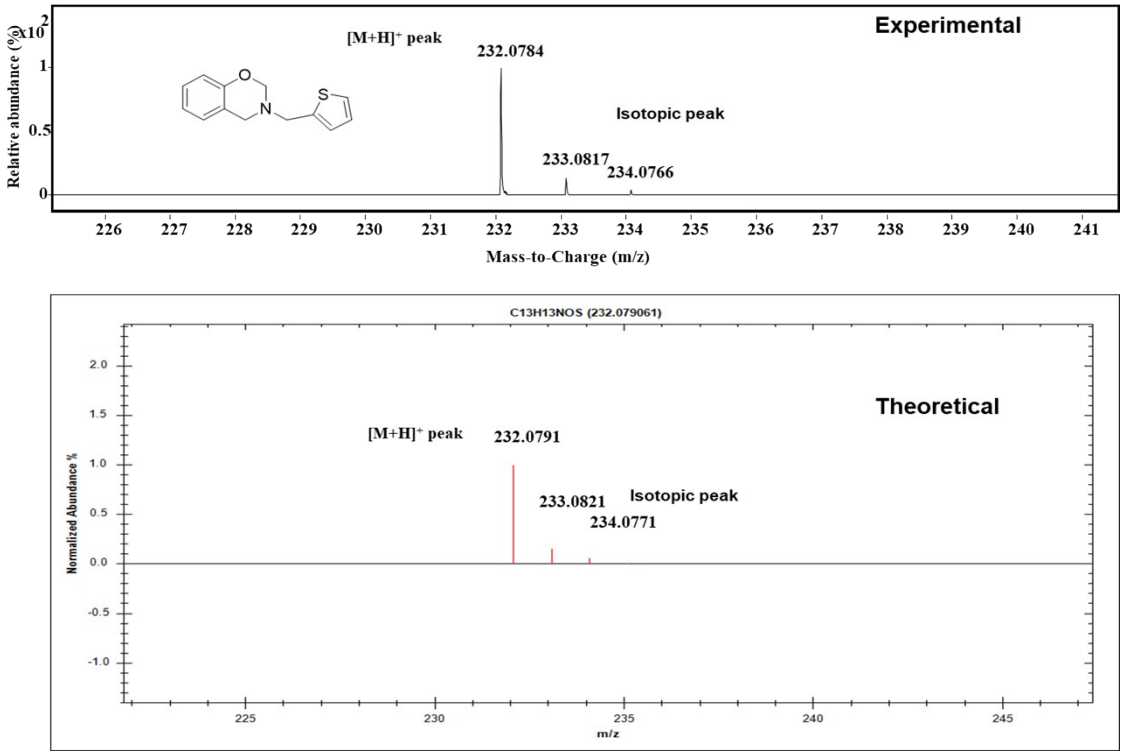


Figure S7. Experimental and theoretical HRMS spectra of PH-ta.

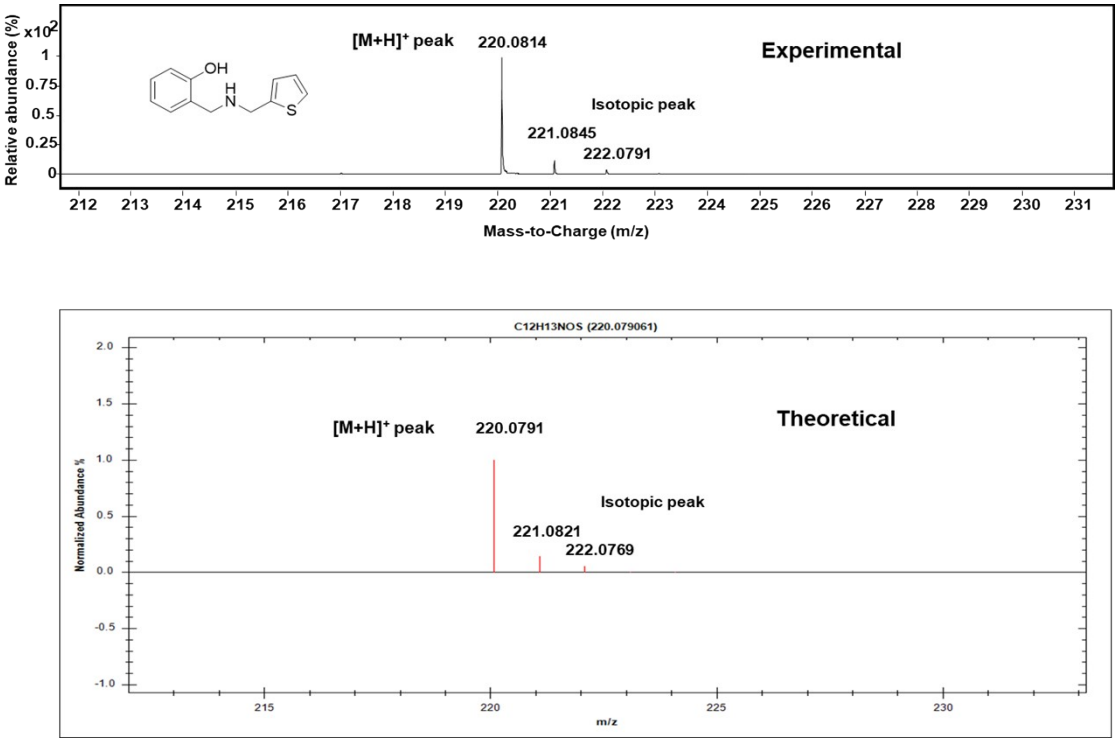


Figure S8. Experimental and theoretical HRMS spectra of 2-hydroxy-N-thiophenylmethylamine [abbreviated as (thiophenyl)aminophenol].

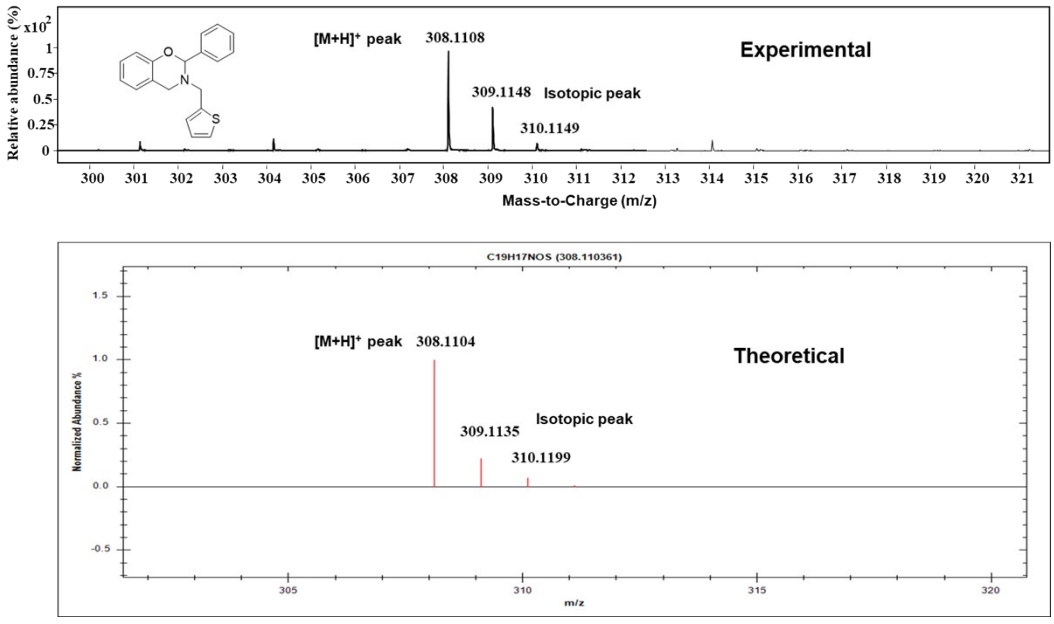


Figure S9. Experimental and theoretical HRMS spectra of PH-ta-[*2*]ph.

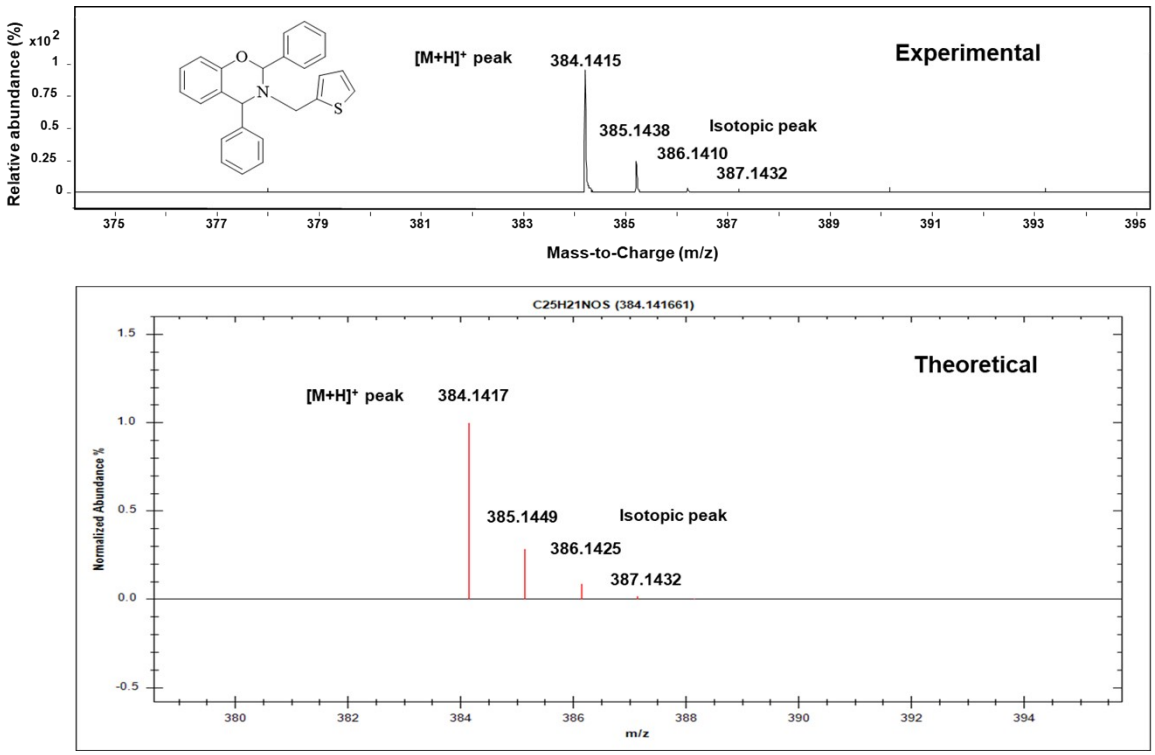


Figure S10. Experimental and theoretical HRMS spectra of PH-ta-[2,*4*]ph.

Raman spectra of the monomers:

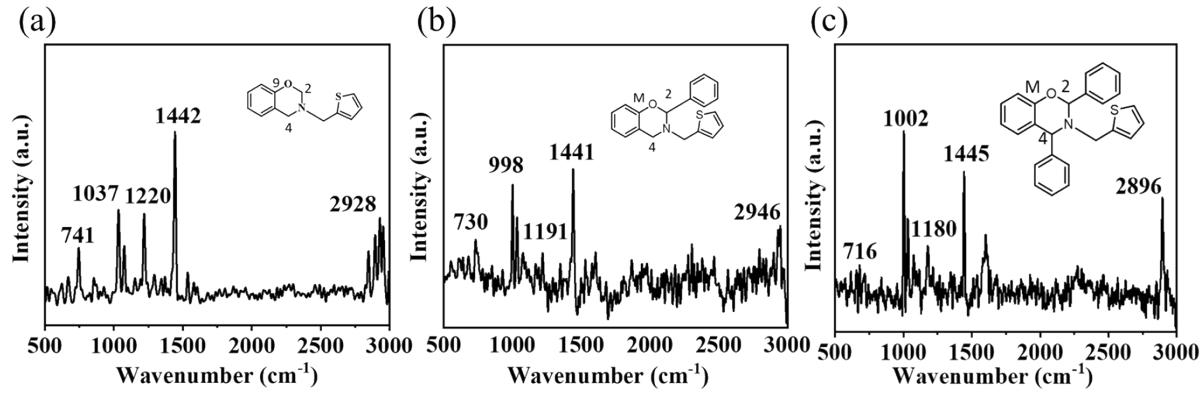


Figure S11. Raman vibration bands in thiophene-based benzoxazines. The characteristics C_4–H stretching (2896-2946 cm^{-1}), H–C_4–H bending (1441-1445 cm^{-1}), C–C–C bend and stretch of phenol ring (1180-1220 cm^{-1}), N–C_4 stretching (998-1037 cm^{-1}), H–C–C bending of phenol ring[4] and/or symmetric mode of the ring[5] (716-741 cm^{-1}) were observed for each type of benzoxazine monomers, viz., (a) PH-ta and (b) PH-ta-[*2*]ph (c) PH-ta-[*2*,*4*]ph.

Crystal data:

Table S1: Crystal data for compound PH-ta-[*2,4*]ph. (CCDC-2131761 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif)

Empirical formula	$C_{25}H_{21}NOS$
Formula weight	383.49
Temperature	289(2)
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	**a** = 11.598(6), **α** = 90° **b** = 9.723(6), **β**= 99.760(18) **c** = 18.055(11), **γ** = 90°
Volume	2007Å^3
Z	4
Density	1.269
Absorption coefficient	0.176
F (000)	988.0
Crystal size	0.210 X 0.140 X 0.098
Theta max	26.665
Theta min	2.289
Reflections collected	31861
Independent reflections	2553
Absorption correction	Multi-scan with SADABS
Max. and min. Transmission	0.9705 and 0.6508
Goodness-of-fit on F^2	1.034
R1	0.0528
wR2	0.1491
R_{int} (all data)	0.0482

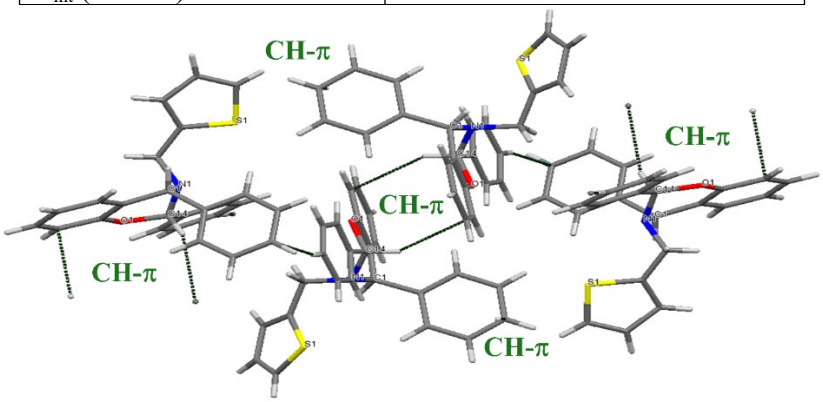
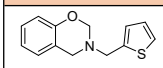
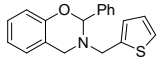
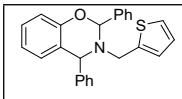


Figure S12. Intermolecular CH-π network observed in the crystal structure of PH-ta-[*2,4*]ph.

DSC data of the monomers:

Table S2: DSC analysis of monomers.

Structure	Name	DSC temperature values (°C)				ΔH (kJ. mol^{-1})	Kissinger Activation Energy E_a (kJ.mol^{-1})
		T_m (Melting temperature)	T_o (Onset temperature)	T_p (Polymerization temperature)	T_o-T_m (Processing window)		
	PH-ta	67	230	242	163	26	79
	PH-ta-*[2]*ph	106	216	224	110	23	92

	PH-ta-*[2,4]*ph	118	196	211	78	34	112

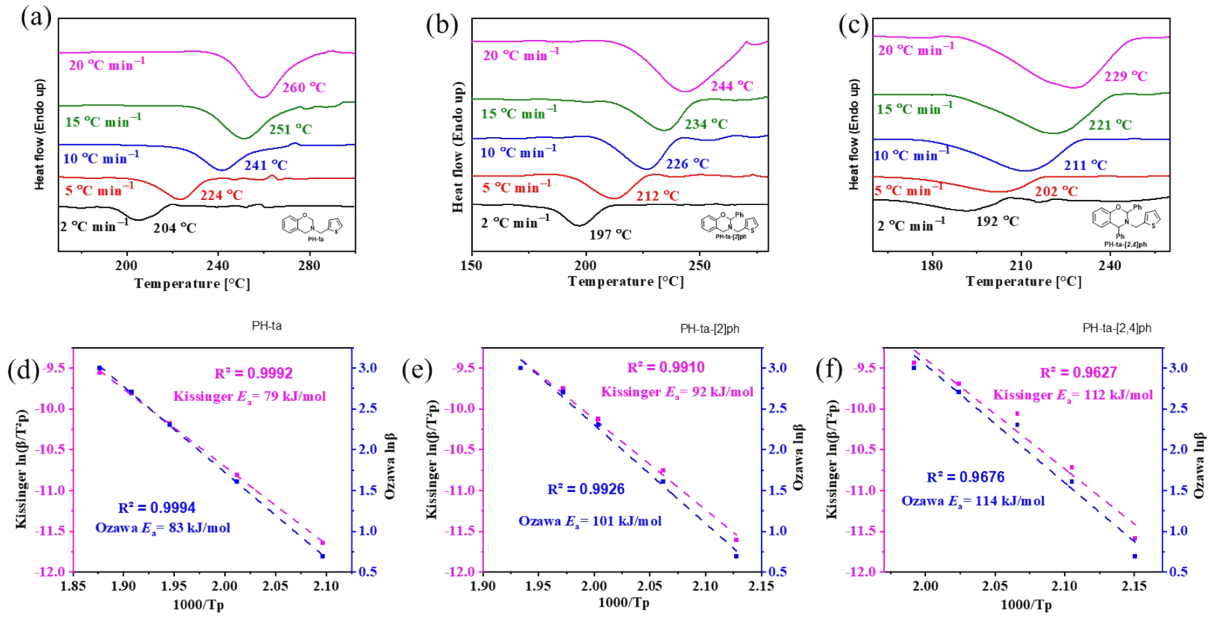


Figure S13. DSC kinetics study: Stacked DSC thermograms of (a) PH-ta and (b) PH-ta-[*2*]ph (c) PH-ta-[*2*,*4*]ph; Plots of activation energy [E_a calculated by Kissinger[6] (pink-colored) and Ozawa[7] (blue-colored) method for polymerization reaction] of (d) PH-ta, (e) PH-ta-[*2*]ph, and (f) PH-ta-[*2*,*4*]ph.

IR kinetics:

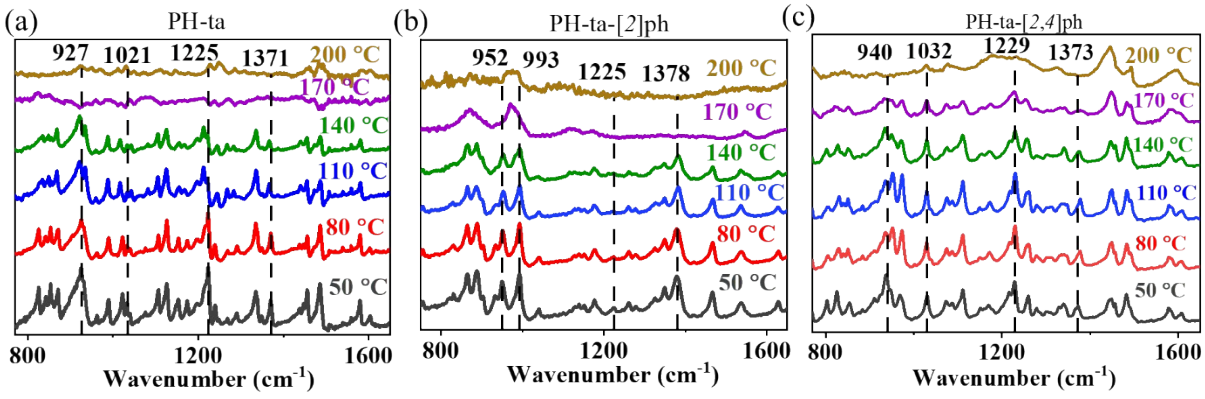


Figure S14. Temperature-dependent variation in the intensity of FTIR bands[4] in thiophene-based benzoxazines. The characteristics C_{Ar}–O–C symmetric (972-993 cm^{-1}) and anti-symmetric (1225-1229 cm^{-1}) stretching bands and oxazine ring skeletal C–H bending out-of-plane vibration (926-940 cm^{-1}), H–C_2–O–C(fused phenyl) torsion (1371-1378 cm^{-1}) were monitored for each type of benzoxazine monomers, viz., (a) PH-ta and (b) PH-ta-[*2*]ph (c) PH-ta-[*2*,*4*]ph.

TGA data of the monomers:

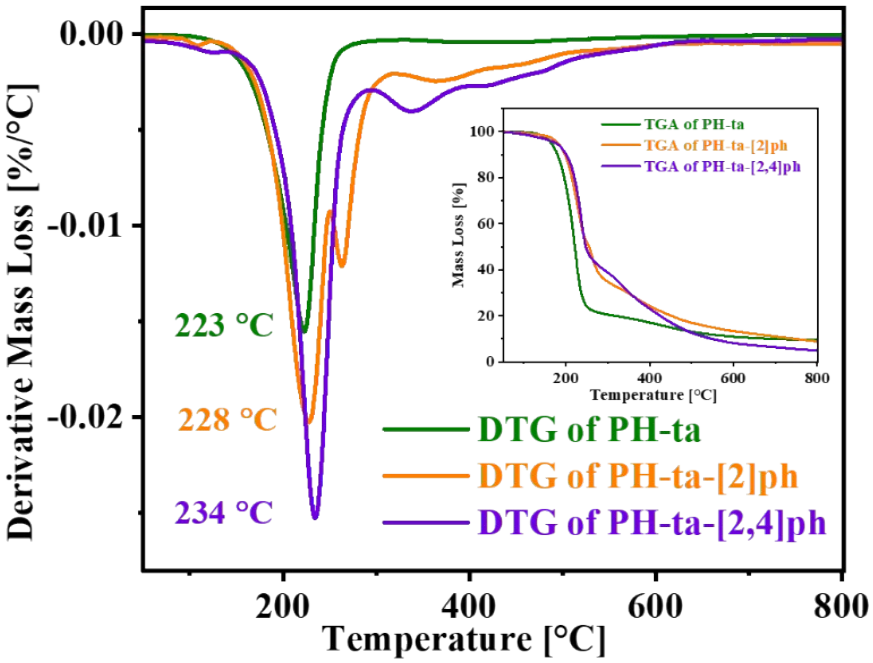


Figure S15. DTG and TGA (inset) thermograms (under N_2 atmosphere, 10 °C.min^{-1}) of PH-ta, PH- ta-[*2*]ph and PH-ta-[*2*,*4*]ph.

2D NOESY spectra of monomers:

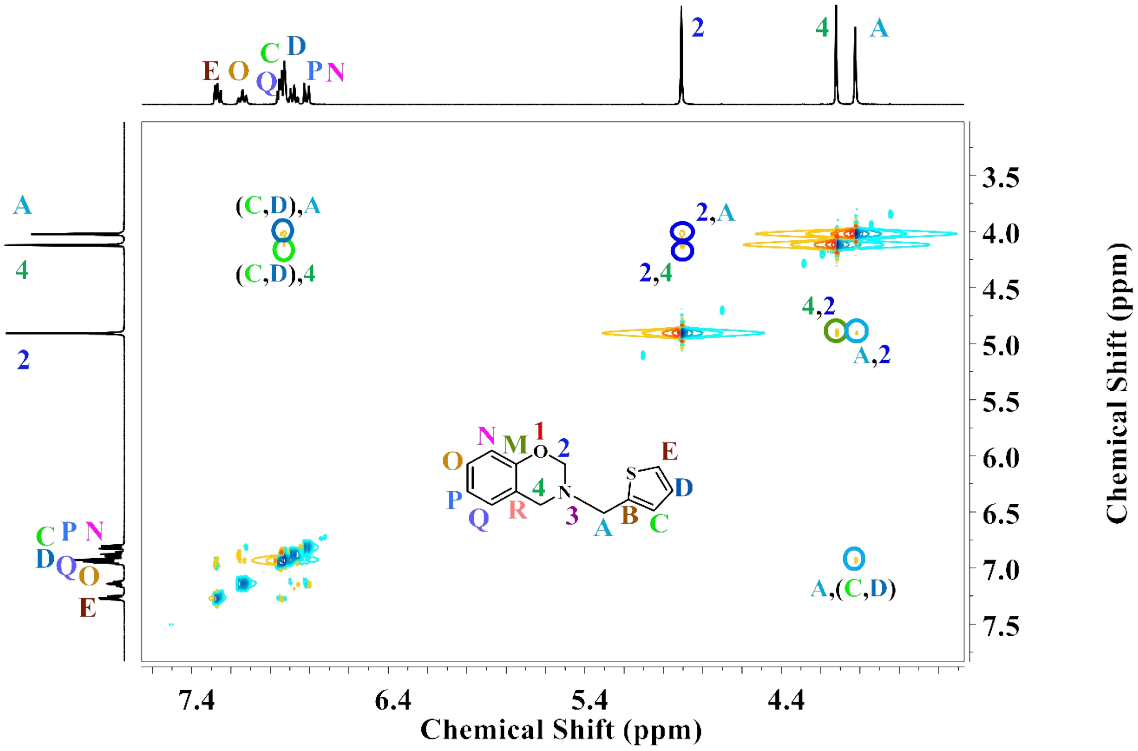


Figure S16. 2D ^{1}H–^{1}H NOESY NMR spectra of PH-ta.

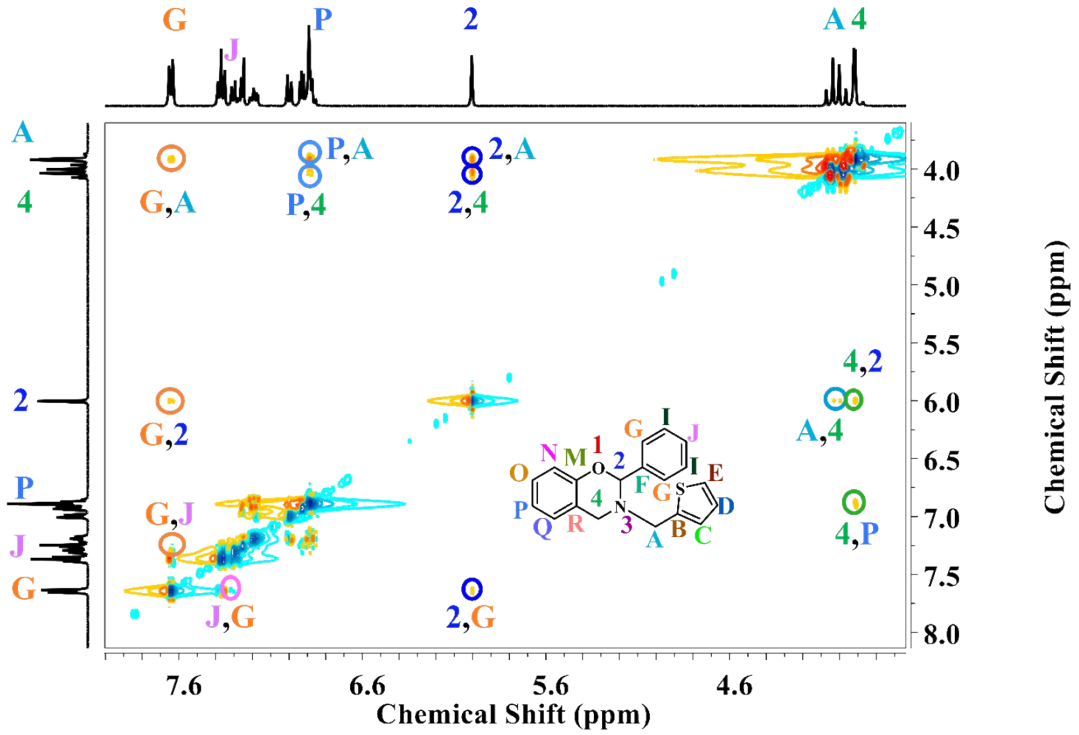


Figure S17. 2D ^{1}H–^{1}H NOESY NMR spectra of PH-ta-[*2*]ph.

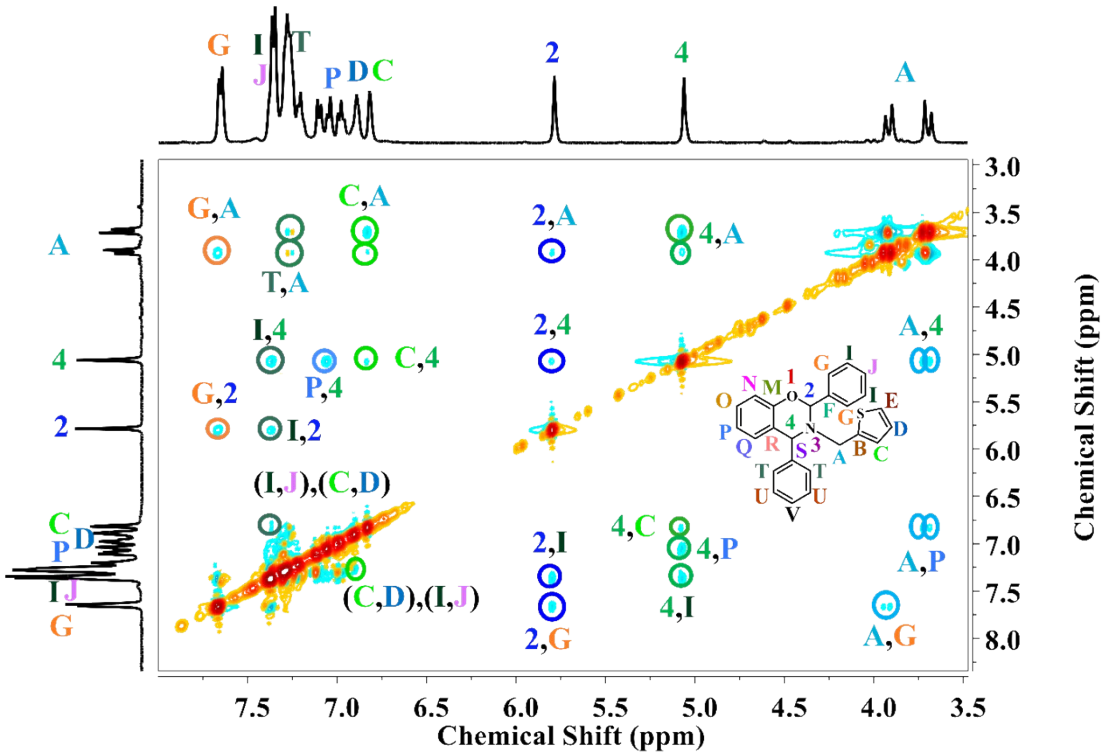


Figure S18. 2D ^{1}H–^{1}H NOESY NMR spectra of PH-ta-[*2*,*4*]ph

Thermogravimetry analysis of polymers:

Table S3: Thermal stability of thiophene (ta) vs furan (fa)[8] based polybenzoxazine.

$T_{d5\%}$: 5% mass loss, $T_{d10\%}$: 10% mass loss, T_{max} determined from DTG traces. Char yield: percentage residual weight left at 800 °C. LOI, (Limiting oxygen index) = 17.5 + 0.4 (char yield, %) [9].

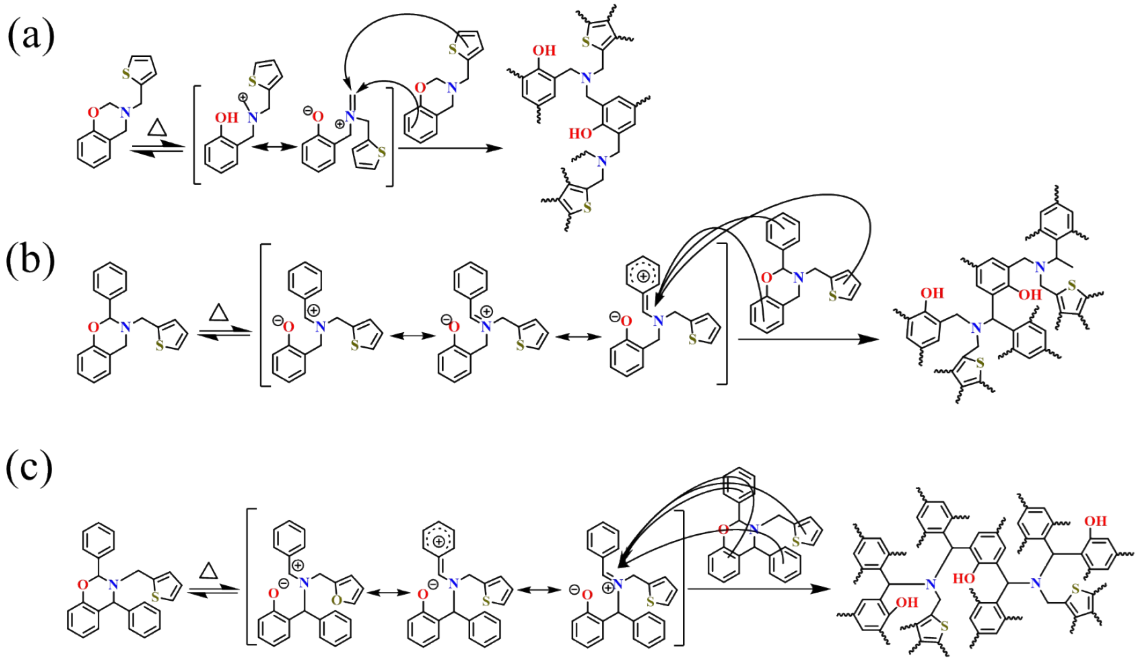


Figure S19: Proposed polymerization mechanism of monomers: (a) PH-ta, (b) PH-ta-[*2*]ph, (c) PH-ta-[*2*,*4*]ph.

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Name	TGA temperature values (°C)			Char Yield (%)	LOI
	$T_{d5\%}$	$T_{d10\%}$	T_{max}		
Poly(PH-fa)	327	380	436	46	35.9
Poly(PH-ta)	334	393	448	57	40.2
Poly(PH-fa-[*2*]ph)	226	320	404	52	38.3
Poly(PH-ta-*[2]*ph)	384	419	455	61	41.8
Poly(PH-fa-[*2,4*]ph)	289	417	474	62	42.3
Poly(PH-ta-[*2,4*]ph)	338	439	542	62	42.3

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