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Optically transparent and thermally stable nonlinear optic chromophores featuring a thieno[2,3-*b*]thiophene donor

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Abstract—A thieno[2,3-*b*]thiophene core has been utilized as a π-donor component to design two series of push–pull thienothiophenes by introducing various acceptor groups either via olefinic or aza-spacers. The molecules show a UV–visible cut-off wavelength below the second harmonic generation (SHG) at $\lambda/2$ of 532 nm, thereby conforming to the nonlinearity–transparency trade-off. Second order molecular nonlinearity, β measured by Hyper-Rayleigh scattering technique was found in the range of $9.58–47.66\times10^{-30}$ esu, while the Kurtz powder technique produced signals of the order of 0.43–1.02 U. Thermal decomposition temperatures measured by differential scanning calorimetry revealed decomposition temperatures≥275 °C, indicating high thermal stability.

1. Introduction

Materials exhibiting large second order nonlinear optic (NLO) properties are in demand due to their potential applications in photonic devices for telecommunications and optical information processing.[1–3] While exhibiting high optical nonlinearity, NLO materials must also possess transparency–nonlinearity trade-off and good thermal stability to be viable for device applications.[4–8] The realization in 1970s that organic chromophores might be more versatile than their inorganic counterparts in terms of high molecular nonlinearity, ultrafast response time, and low costs has stimulated unprecedented development in the field of organic based NLO systems.[9–11]

Although, increasing π-conjugation generally translates into higher molecular hyperpolarizability, the advantage is often offset by lower stability and serious compromise on optical transparency. One of the recent strategies to contain these drawbacks is to replace aromatics with less resonance stabilized heteroaromatic nuclei as the π-bridges in donor–π–acceptor (D–π–A) systems.[12–15] The hetero-ring chromophores, compared to their aromatic counterparts, not only possess higher hyperpolarizability but they also display better thermal stability.[16–20] In particular, thiophene based D–π–A chromophores, including dithienyl push–pull systems have been extensively investigated, many showing good NLO characteristics.[21,22] Moderate levels of first hyperpolarizability have also been reported for NLO systems derived from thieno[3,2-*b*]thiophenes.[23–25] In the context of our interest in organic NLO systems,[26,27] we recently described the first application of thieno[2,3-*b*]thiophene in the design of a novel NLO system by incorporating this nucleus within an unsymmetrically functionalized cyclophane.[28] Presently, we have extended the scope of thieno[2,3-*b*]thiophene toward the creation of push–pull structures with a view to investigate their potential in the NLO field.

2. Results and discussion

Most known organic NLO phores utilize aromatics or heteroaromatic rings as the π-conjugation bridges. However, in contrast, we decided to exploit the 10π electron rich thieno[2,3-*b*]thiophene (**TT**) core in capacity as the donor component and to introduce various π-electron acceptors at the C2 position of **TT** through olefinic or aza-spacers to access the corresponding push–pull chromophores, **4a–f** and **7a–d**, respectively. We envisaged that the high lying HOMO of thienothiophene[29] would effectively interact with the low lying LUMO of the π-attached acceptors to generate sufficiently polarized frameworks necessary for exhibiting the NLO effects. Further, it was anticipated that in the absence of an additional donor chromophore, the intramolecular charge transfer (ICT) transitions in **4a–f** and **7a–d** should be restricted below the simple harmonic generation

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Keywords: Nonlinear optics; Push–pull thieno[2,3-*b*]thiophenes; Synthesis; UV–visible; First hyperpolarizability; Hyper-Rayleigh scattering technique; Kurtz powder method; Thermal decomposition.

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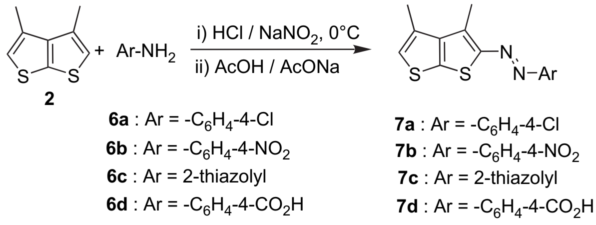
($\lambda/2$ of 532 nm) to avoid reabsorption of the simple harmonic generation. Herein, we describe the synthesis, optical properties, and thermal stability of **4a–f** and **7a–d**.

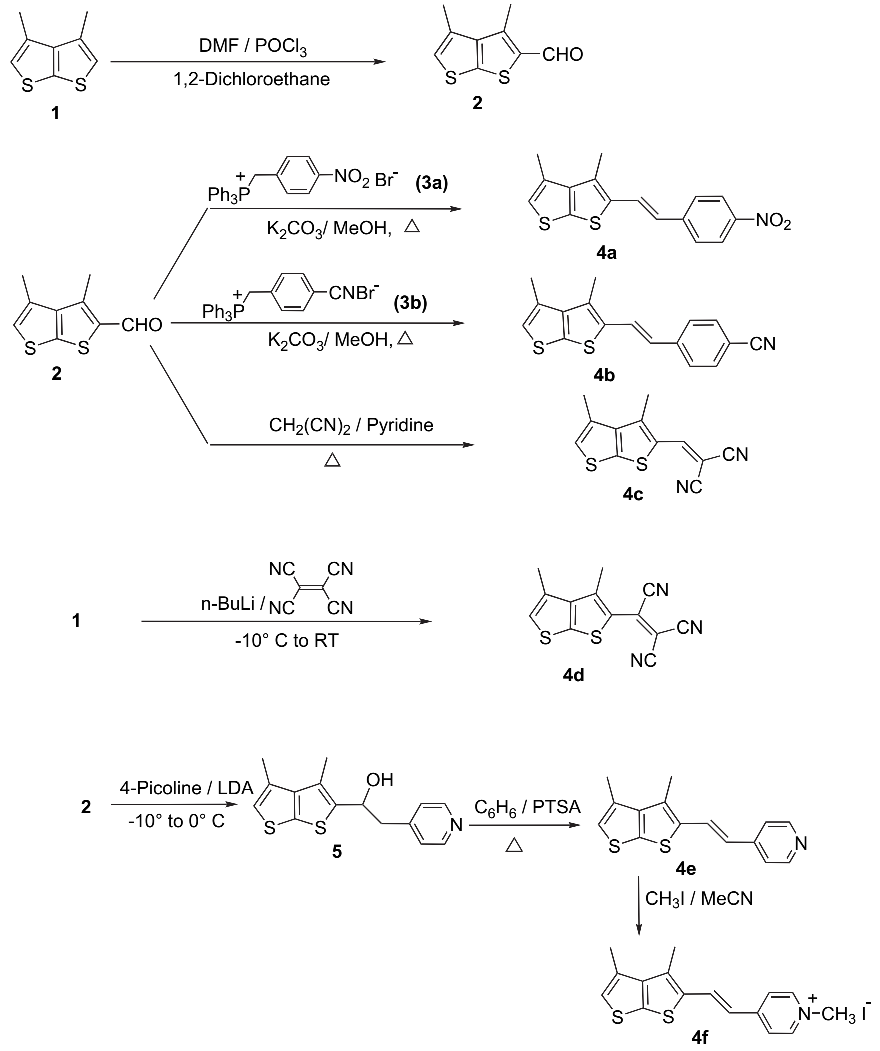
2.1. Synthesis of push–pull thienothiophene chromophores

The synthetic approaches used to synthesize the first series of **TT**–π–A, **4a–f** are depicted in Scheme 1. The starting material, 2-formyl-3,4-dimethylthieno[2,3-*b*]thiophene **2** was readily prepared in multigram quantity by formylation of known thieno[2,3-*b*]thiophene **1** using our recently described protocol.[28] Wittig condensation of **2** with phosphonium salts **3a** and **3b** yielded cis/trans mixtures from which the desired, major *E* isomers **4a** and **4b** were readily isolated by recrystallization. Dicyanovinyl substituted **TT**, **4c** was prepared via the standard Knoevenagel protocol[28] in excellent yield and tricyanovinyl chromophore was introduced via the lithiation protocol (treatment of **1** with *n*-BuLi, followed by reaction with TCNE) to access tricyanovinyl analog **4d**. Thienothiophene chromophore **4e** carrying a 4-vinylpyridyl group was prepared in two steps by condensing **2** with 4-picoline under LDA/THF conditions, followed by dehydration of the resulting carbinol **5** with *p*-toluenesulfonic acid in refluxing benzene. In order to enhance the NLO properties, **4e** was quaternized with CH_3I to form the pyridinium salt **4f** in excellent yield.

As shown in Scheme 2, aza-coupling of diazonium salts derived from a few acceptor amines (**6a–d**) with thienothiophene **1** smoothly led to the synthesis of deep yellow to red aza-conjugated systems **7a–d** in good yields. The successful diazonium coupling clearly implies the high π-electron donating ability of the thieno[2,3-*b*]thiophene ring and constitutes the first report on the aza-coupling of this ring system. The structures of target NLO phores **4a–f** and **7a–d** have been fully characterized by elemental analysis and spectral data (see Section 4).



Scheme 2. Synthesis of push–pull thienothiophenes **7a–d**.



Scheme 1. Synthesis of push–pull thienothiophenes **4a–f**.

2.2. Electronic spectra

The UV–visible spectra of π-conjugated thieno[2,3-*b*]thiophenes, **4a–f** and **7a–d** recorded in $CHCl_3$ solvent are shown in Table 1. For illustration, UV–visible spectra for **4a–f** and **7a–d** are depicted in Figures 1 and 2, respectively. The main absorption bands for **4a–f** and **7a–d** are located in the range of 367–442 nm and 382–431 nm, respectively, depending on the nature of the π-spacer and the attached electron acceptor groups. These absorption bands are attributable to the ICT transitions. Consistent with the increase in the number of electron withdrawing –CN groups, the ICT bands in the cyano series, **4b–d** are red shifted in the order **4b**<**4c**<**4d**. The absorption maxima for the tricyano compound **4d** and that of the 4-nitrostyryl analog **4a** appear at nearly similar λ_{max} (around 407 nm), thereby suggesting their comparable electron withdrawing properties. Conversion of neutral **4e** to ionic *N*-quaternized salt **4f** led to a bathochromic shift of the ICT band from 367.5 nm in **4e** to 442 nm in **4f**. The red shift is in accord with the increased π-acceptor property of the pyridinium ring relative to the neutral pyridyl analog.[27] The following comparisons serve to indicate that the π-donor ability of thieno[2,3-*b*]thiophene ring is superior than that of the thiophene ring. For instance, the λ_{max} for **4e** and **4f** appear at longer wavelengths (367 and 442 nm, see Table 1), whereas for the case of known thiophene analogs, 1-(2-thienyl)-2-(4-pyridyl)ethene and its *N*-methylpyridinium salt, the absorption maxima are reported at lower wavelengths at 332 and 377 nm, respectively.[30]

In accord with the literature report,[31] available comparisons in the **TT** chromophores indicate that the aza-bridge seems to offer a better charge redistribution than the olefinic bridge. Thus, the transition energy for aza-nitrophenyl system **7b** is found to be lower (λ_{max} at 422 nm) than that observed for the corresponding nitrostyryl analog **4a** (λ_{max} 407 nm). Also, the excitation energy for **7a**, carrying a weakly electron withdrawing 4-chlorophenyl group is lower (λ_{max} at 382 nm) than that of **4b**, possessing a relatively stronger acceptor, 4-cyanophenyl chromophore (λ_{max} at 371 nm). It is worth noting that no absorption ($\lambda_{cut\text{-}off}$ at 520 nm) is discernible in the region of SHG at 532 nm for molecules **5a–f** and **7a–d** (see Figs. 1 and 2). Accordingly, these molecules fairly well conform to the transparency–nonlinearity trade-off.

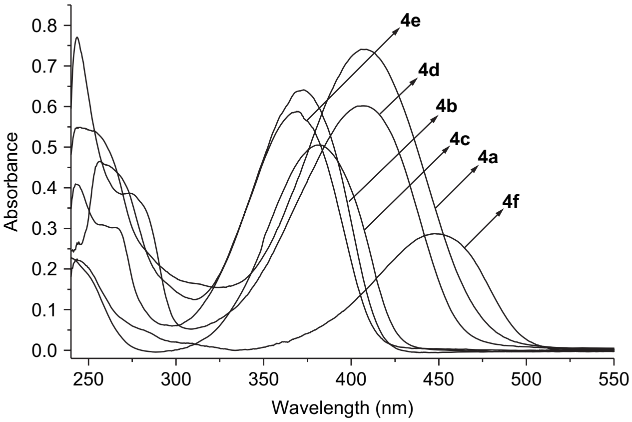


Figure 1. UV–visible spectra of **4a–f** in $CHCl_3$.

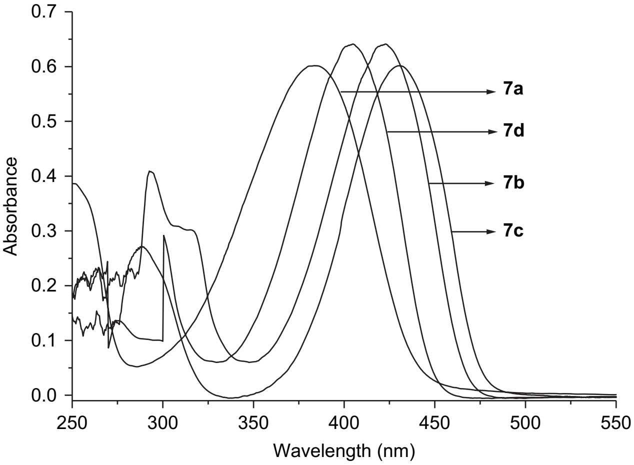


Figure 2. UV–visible spectra of **7a–d** in $CHCl_3$.

2.3. Molecular hyperpolarizability and thermal stability

The first hyperpolarizability β of the presently synthesized 'push–pull' thienothiophenes was experimentally determined using the Hyper-Rayleigh scattering (HRS) technique in $CHCl_3$ solution using the fundamental excitation wavelength of 1064 nm by applying the external reference method using *p*-nitroaniline as the reference standard.[32] The β values were derived using the method reported by

Table 1. UV–visible, first hyperpolarizability β, static hyperpolarizability β(0), Kurtz powder data, and thermal decomposition T_d of **4a–f** and **7a–d**

Compounds	$CHCl_3$ λ_{max} (nm)	$\beta^a \times 10^{-30}$ esu	$\beta(0) \times 10^{-30}$ esu	Kurtz powder efficiency[b] (U)	Thermal stability T_d (°C)
4a	407	39.59	14.01	0.57	345
4b	371.5	9.59	4.31	0.49	389
4c[27]	380.5	9.58	3.82	1.03	325
4d	408	44.03	15.58	0.78	370
4e	367.5	10.05	4.62	0.68	275
4f	442	29.01	7.17	0.65	363
7a	382	34.89	13.59	0.43	371
7b	422	40.33	10.44	0.56	285
7c	431	46.86	13.32	0.54	435
7d	404	47.66	17.33	0.70	310

[a] In the external reference method, the measured β values were calibrated against *p*-nitroaniline (17.8×10^{-30} esu) in chloroform.

[b] The values of Kurtz powder method are with respect to urea as 1 U.

Parsoons et al.,[33] whereas $\beta(0)$ were calculated by using a two state model.[34] Hyperpolarizability values together with data on powdered SHG efficiency measured by the Kurtz powder method are summarized in Table 1. 4-Cyanostyryl-**TT**, **4b** and dicyanovinyl-**TT**, **4c** both showed moderate β values of around 9.5×10^{-30} esu. In contrast to **4b** or **4c**, the tricyanovinyl chromophore, **4d**, in accord with the powerful acceptor property of tricyanovinyl chromophore, displayed nearly four times higher β of 44.03×10^{-30} esu. As expected, the 4-nitrostyryl-**TT**, **4a** having a similar λ_{max} as that of **4d**, exhibited a comparable β of 39.5×10^{-30} esu. The first hyperpolarizability β for the pyridyl-**TT**, **4e** was found to be 10×10^{-30} esu, which increased almost three times to 29×10^{-30} esu in the corresponding *N*-alkylpyridinium salt **4f**. This result clearly reflects the higher acceptor strength of the pyridinium ring vis-à-vis the neutral pyridine ring. The static hyperpolarizability $\beta(0)$, being a more reliable measure of nonlinear response was found to be the highest for **4a** and **4d** (14×10^{-30} and 15.6×10^{-30} esu, Table 1) carrying 4-nitrostyryl and tricyanovinyl chromophores, respectively.

Among the aza-TT systems, **7a–d**, β was found to be in the range of $34.8–47.7\times10^{-30}$ esu. With respect to the π-attached acceptor chromophores, the β in the above series followed the order 4-Cl–Ph<4-NO–Ph <thiazole<4-HO_2CPh. Interestingly, the highest β in the aza-**TT** series is recorded for the case of **7d** although its λ_{max} is lower (404 nm) compared to those of **7b** and **7c** (422 and 431 nm, respectively). This observation implies that factor(s) other than molecular polarizability contribute in part to the nonlinear optic effect. Consistent with the higher polarizability of the aza-push–pull systems over the olefinic analogs,[35] we find β for aza-**TT** systems, **7a–d** to be comparable or better than those measured for the olefinic-**TT**, **4a–f**. In terms of $\beta(0)$, NLO phores, **7d** showed the highest value of 17.33×10^{-30} esu. It is worth noting that for a number of **TT**-based NLO systems, the β values are substantially higher (up to 47.66×10^{-30} esu, see Table 1) compared to the well-known NLO prototype, *p*-nitroaniline (17.8×10^{-30} esu). No photodecomposition of **TT** chromophores was noticed since the samples recovered after repeated laser excitations showed FTIR spectra are identical to those of the un-irradiated samples.

Interestingly, all the presently synthesized systems exhibited SHG signals by Kurtz powder test with efficiency of the order of 0.43–1.03 U. Since, crystals suitable for single X-ray crystal analysis could not be grown for **4a–f** and **7a–d**, we are presently unable to comment on the structural features responsible for the origin of macroscopic nonlinearity in these systems. Despite the powder efficiency being modest, the detection of positive SHG signals for NLO phores **4a–f** and **7a–d** may indicate non-centrosymmetric orientation in the solid state.[36] As shown in Table 1, no apparent correlation is found between the β derived from the HRS and SHG efficiency obtained by Kurtz test. The absence of correlation between the two methods may not be surprising on the ground that unlike the HRS, which is a solution measurement, the Kurtz method, being a solid state technique is subjected to wide variations depending upon the nature of the space group, sizes and quality of crystals.[37,38] The thermal decomposition temperatures (T_d) of **TT** NLO phores were measured by differential scanning calorimetry and the results are cited in Table 1. Interestingly, all the **TT** chromophores investigated revealed high thermal stability and T_d's are higher than 275 °C. The thermal stability of majority of **TT** NLO phores are superior to that reported for the well-known NLO prototype, DANS (T_d=290 °C).[39]

3. Conclusion

Push–pull chromophores **4a–f** and **7a–d** bearing thieno[2,3-*b*]thiophene motif as the donor component and π-deficient aromatics/heteroaromatic as the acceptors have been designed using straightforward synthetic protocols. It is noteworthy that despite the absence of any additional donor group, some of the **TT** NLO phores exhibit substantial β up to 48×10^{-30} esu. In accord with our expectations, the absence of any additional donor in the **TT** NLO phores leads to anticipated restriction of the λ_{ICT} below the second harmonic generation, a feature, which is of key importance for device fabrications. Despite the first hyperpolarizability values for **TT** NLO phores being modest by current standard, their optical transparency and high thermal stability render push–pull thienothiophenes potentially interesting materials in NLO applications.

4. Experimental

4.1. General

The chemicals and spectral grade solvents were purchased from S/D. Fine Chemicals (India) and used as received. IR spectra were recorded on a Shimadzu FTIR-420 spectrophotometer. ^1H NMR spectra were scanned in $CDCl_3$ using Bruker 300 MHz spectrometer with TMS as an internal standard. Coupling constants *J* are given in hertz. Elemental analyses were done on Carlo Ebra instrument EA-1108 Elemental analyzer. UV–vis spectra were recorded on Jasco V-530 UV–vis spectrophotometer. The β values were derived using the Hyper-Rayleigh scattering (HRS) technique in $CHCl_3$ solution at the fundamental excitation wavelength of 1064 nm by using *p*-nitroaniline (17.8×10^{-30} esu in chloroform) as the reference standard.[33] The static hyperpolarizability values $\beta(0)$ were calculated by applying a two state model[34] as per the expression given in Eq. 1.[34]

$$\beta/\beta_0=(\omega_0)^4/\left[\left(\omega_0^2-\omega^2\right)\left(\omega_0^2-4\omega^2\right)\right] \tag{1}$$

where ω_0 is the single photon absorption maximum of the molecule in wave numbers, and ω is the laser fundamental. The hyperpolarizability values are uncorrected for any possible two photon fluorescence.

4.1.1. Preparation of 4-nitrostyryl analog 4a. Thienothiophene 2-carboxaldehyde **2** (0.196 g, 1 mmol) and triphenyl phosphonium salt **3a** (0.478 g, 1 mmol) were dissolved in dry methanol, to which anhyd K_2CO_3 (1 g) was added. The reaction mixture was refluxed for 24 h whereby the color of the reaction mixture changed from light yellow to red. After cooling, the reaction mixture was poured into water and the precipitated solid filtered off, washed with water and then crystallized from ethanol to give **4a** as yellow crystals, mp 237–239 °C in 80% yield. Anal. Calcd for $C_{16}H_{13}NO_2S_2$: C, 60.95; H, 4.13; N, 4.44; S, 20.32. Found: C, 60.71; H, 4.03; N, 4.40; S, 20.56. IR (KBr; ν cm^{-1}): 3150, 2950, 1620, 1590, 1510, 1480, 1390, 1340, 1105, 940, 870, 840, 820, 750, 720, 690. ^{1}H NMR (300 MHz; CDCl$_3$): δ 2.51 (3H, s), 2.58 (3H, s), 6.89 (1H, s), 6.82 (1H, d, J=16 Hz), 7.47 (1H, d, J=16 Hz), 7.58 (2H, d, J=8 Hz), 8.20 (2H, d, J=8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.355, 15.910, 123.719, 124.367, 124.619, 125.183, 126.563, 131.474, 138.292, 144.012.

4.1.2. Preparation of 4-cyanostyryl analog 4b. Thienothiophene 2-carboxaldehyde **2** (0.196 g, 1 mmol) and triphenyl phosphonium salt **3b** (0.458 g, 1 mmol) were reacted as described above. The crude product was recrystallized from ethanol to give **4b** as yellow crystals, mp 196–198 °C in 75% yield. Anal. Calcd for $C_{17}H_{13}NS_2$: C, 69.15; H, 4.41; N, 4.75; S, 21.69. Found: C, 68.89; H, 4.38; N, 4.61; S, 21.48. IR (KBr; ν cm^{-1}): 3100, 2950, 2200, 1620, 1600, 1420, 1410, 1390, 930, 860, 840, 810, 720, 680, 640. ^{1}H NMR (300 MHz; CDCl$_3$): δ 2.50 (3H, s), 2.56 (3H, s), 6.88 (1H, s), 6.76 (1H, d, J=16 Hz), 7.40 (1H, d, J=16 Hz), 7.53 (2H, d, J=8 Hz), 7.62 (2H, d, J=8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.209, 15.810, 110.212, 119.211, 123.543, 124.214, 125.037, 126.532, 128.637, 132.549, 141.860.

4.1.3. Preparation of tricyanovinyl analog 4d. A solution of thienothiophene **1** (0.168 g, 10 mmol) in dry THF (20 mL) was cooled to −10 °C and *n*-BuLi (1.6 M, 2 mL) was added under a continuous flow of N_2. Stirring was continued for 40 min and then tetracyanoethylene (0.128 g, 1 mmol) dissolved in 10 mL of dry THF was added dropwise. Reaction mixture was stirred for 30 min and temperature was allowed to rise to 0 °C. The reaction mixture was concentrated, diluted with water, and extracted with chloroform. The organic layer was washed with water and dried over anhyd Na_2SO_4. The crude product obtained upon solvent removal was purified by chromatography on silica gel (eluant: pet. ether–chloroform 30:70) to afford **4d** as deep yellow solid, mp 289–291 °C in 25% yield. Anal. Calcd for $C_{13}H_7N_3S_2$: C, 57.99; H, 2.60; N, 15.61; S, 23.79. Found: C, 57.81; H, 2.72; N, 15.41; S, 23.91. IR (KBr; ν cm^{-1}): 3100, 2900, 2200, 1540, 1510, 1490, 1450, 1420, 1370, 1260, 1220, 1040, 830, 760, 770. ^{1}H NMR (300 MHz; CDCl$_3$): δ 2.54 (3H, s), 2.57 (3H, s), 6.96 (1H, s). ^{13}C NMR (100 MHz, CDCl$_3$): δ 16.085, 16.360, 110.160, 112.043, 112.310, 113.271, 126.830, 132.237, 142.944, 147.825, 148.069.

4.1.4. Preparation of pyridylvinyl analog 4e. To a solution of LDA (2 M in THF, 1.25 mL) was added a solution of γ-picoline (0.1 mL, 1 mmol) dissolved in dry THF (5 mL) at 0 °C under an atmosphere of N_2. The reaction mixture was stirred for 30 min and a solution of aldehyde **2** (0.196 g, 1 mmol) in dry THF (10 mL) was added dropwise for 10 min. The reaction mixture was allowed to warm to room temperature and left overnight. The reaction mixture was poured onto crushed ice and extracted with dichloromethane, washed with water, and dried over anhyd Na_2SO_4. The crude product obtained on concentration was purified by silica gel chromatography (eluant: pet. ether–chloroform 30:70) to give carbinol **5** as a brown solid, mp 179–181 °C in 65% yield. Anal. Calcd for $C_{15}H_{15}NOS_2$: C, 62.28; H, 5.19; N, 4.84; S, 22.15. Found C, 62.30; H, 5.32; N, 4.71; S, 22.15. IR (KBr; ν cm^{-1}): 3200, 3100, 2950, 1600, 1560, 1420, 1410, 1300, 1070, 100, 800, 740. ^{1}H NMR (300 MHz; CDCl$_3$): δ 2.2 (3H, s), 2.4 (3H, s), 3.1 (2H, d, J=9.5 Hz), 5.2 (1H, t, J=9.5 Hz), 6.8 (1H, s), 7.1 (2H, d, J=6 Hz), 7.3 (1H, s), 8.4 (2H, d, J=6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.061, 15.843, 45.082, 69.110, 122.980, 124.991, 126.614, 131.022, 135.988, 143.653, 146.321, 147.237, 149.283.

Carbinol **5** (0.58 mg, 0.5 mmol) was dissolved in dry benzene (10 mL) containing a catalytic amount of *p*-toluenesulfonic acid (50 mg). The reaction was heated on water bath for 3 h to effect dehydration. The initial yellow color of the reaction turned gradually reddish indicating the formation of conjugated product **4e**. The reaction was diluted with water, basified with satd Na_2CO_3 and extracted with dichloromethane. The organic extract, after washing with water was dried over anhyd Na_2SO_4 and concentrated to afford the product as a red solid. Purification on SiO_2 column (elution with pet. ether–chloroform 50:50) gave **4e** as a deep yellow solid, mp 189–191 °C in 90% yield.

Anal. Calcd for $C_{15}H_{13}NS_2$: C, 66.42; H, 4.80; N, 5.17; S, 23.62. Found C, 66.27; H, 4.64; N, 5.33; S, 23.85. IR (KBr; ν cm^{-1}): 3150, 2900, 1620, 1590, 1550, 1480, 1420, 1380, 1290, 1220, 1200, 1020, 990, 940, 800. ^{1}H NMR (300 MHz; CDCl$_3$): δ 2.50 (3H, s), 2.55 (3H, s), 6.88 (1H, s), 6.91 (1H, d, J=16 Hz), 7.50 (1H, d, J=16 Hz), 7.32 (2H, d, J=6 Hz), 8.55 (2H, d, J=6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.748, 15.373, 121.003, 123.437, 124.918, 125.242, 126.579, 132.785, 137.385, 145.124, 149.241.

4.1.5. Preparation of *N*-methyl pyridinium thienothiophene analog 4f. Pyridylvinyl analog **4e** (0.271 g, 1 mmol) was dissolved in dry acetonitrile (2 mL) to which an excess of methyl iodide (0.5 mL) was added. The reaction mixture was kept at room temperature for 48 h and the separated solid product was filtered, washed with cold ethanol, and dried under vacuum to afford **4f** as a reddish solid, mp 334 °C (dec) in quantitative yield. Anal. Calcd for $C_{16}H_{16}NS_2I$: C, 46.49; H, 3.87; S, 15.49; N, 3.39; I, 30.75. Found: C, 46.21; H, 3.69; S, 15.60; N, 3.56; I, 30.70. IR (KBr; ν cm^{-1}): 3100, 2950, 1640, 1600, 1580, 1520, 1480, 1420, 1380, 1300, 1280, 1210, 1180, 1150, 1050, 940, 820. ^{1}H NMR (300 MHz; DMSO): δ 2.48 (3H, s), 2.68 (3H, s), 4.23 (3H, s), 6.98 (1H, d, J=16 Hz), δ 7.23 (1H, s), 8.25 (1H, d, J=16 Hz), 8.29 (2H, d, J=7 Hz), 8.78 (2H, d, J=7 Hz). ^{13}C NMR (100 MHz, DMSO): δ 13.748, 15.492, 47.542, 120.446, 123.098, 124.842, 126.776, 130.421, 131.283, 132.557, 135.908, 137.385, 145.154, 152.862.

4.2. Synthesis of aza-thienothiophenes 7a–d: typical procedure

To concd sulfuric acid (4 mL) was added a given aromatic amine (**6a–d**) (2.5 mmol) and the reaction was cooled to 0 °C. A solution of sodium nitrite (206 mg, 3 mmol) prepared in 2 mL of water was added slowly and the reaction maintained at 0 °C for 1 h. To this mixture, a solution of thieno[2,3-*b*]thiophene **1** (336 mg, 2 mmol) in 25 mL of glacial acetic acid was added at 0–5 °C with stirring. Sodium acetate (1.0 g) was added and the reaction was stirred for 2 h. The reaction mixture was then poured into water and neutralized with aq sodium carbonate. The resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography giving orange to reddish solid.

4.2.1. Synthesis of aza-thienothiophenes 7a. Yield: 65%, mp 180–183 °C. Anal. Calcd for $C_{14}H_{11}N_2S_2Cl$: C, 54.81; H, 3.59; N, 9.13; S, 20.88; Cl, 11.58. Found: C, 54.65; H, 3.50; N, 9.01; S, 20.78; Cl, 11.50. IR (KBr; ν cm^{-1}): 3092, 2915, 1606, 1575, 1519, 1493, 1342, 1267, 1142, 1109, 1065, 989, 892, 833, 730, 682. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.45 (3H, s), 2.85 (3H, s), 6.80 (1H, s), 7.30 (2H, d, J=7.80 Hz), 7.65 (2H, d, J=7.80 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.225, 15.633, 120.129, 123.991, 124.769, 126.772, 129.199, 129.577, 130.566, 132.508, 136.686.

4.2.2. Synthesis of aza-thienothiophenes 7b. Yield: 69%, mp 205–207 °C. Anal. Calcd for $C_{14}H_{11}N_3O_2S_2$: C, 52.99; H, 3.47; N, 13.25; S, 20.19. Found: C, 52.78; H, 3.40; N, 13.02; S, 20.02. IR (KBr; ν cm^{-1}): 3095, 2920, 1588, 1518, 1324, 1149, 1105, 879, 857, 776, 752. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.52 (3H, s), 2.80 (s, 3H), 6.75 (1H, s), 7.21 (2H, d, J=8.0 Hz), 7.80 (2H, d, J=8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.234, 15.639, 120.218, 127.182, 129.681, 132.583, 136.789.

4.2.3. Synthesis of aza-thienothiophenes 7c. Yield: 70%, mp 168–171 °C. Anal. Calcd for $C_{11}H_9N_3S_3$: C, 47.31; H, 3.22; N, 15.05; S, 34.41. Found: C, 47.15; H, 3.10; N, 14.88; S, 34.24. IR (KBr; ν cm^{-1}): 3094, 2920, 2800, 1601, 1580, 1500, 1480, 1440, 1420, 1380, 1340, 1310, 1295, 1240, 1150, 1140, 1040, 1020, 880, 870, 798, 740, 720. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.52 (3H, s), 2.75 (3H, s), 6.90 (1H, s), 7.20 (1H, d, J=3.9 Hz), 7.55 (1H, d, J=3.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.426, 15.178, 121.873, 125.455, 132.261, 141.899, 143.792, 145.831.

4.2.4. Synthesis of aza-thienothiophenes 7d. Yield: 60%, mp 190–193 °C. Anal. Calcd for $C_{15}H_{12}N_2O_2S_2$: C, 56.96; H, 3.79; N, 8.86; S, 20.25. Found: C, 56.72; H, 3.69; N, 8.76; S, 20.05. IR (KBr; ν cm^{-1}): 3466, 2920, 1682, 1601, 1575, 1417, 1391, 1343, 1285, 1144, 862, 797, 773. ^{1}H NMR (300 MHz; DMSO): δ 2.40 (3H, s), 2.60 (3H, s), 6.80 (1H, s), 7.05 (2H, d, J=7.9 Hz), 7.85 (2H, d, J=7.9 Hz), 12.80 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.334, 15.212, 122.177, 124.742, 130.542, 131.643, 132.173, 139.647, 142.281, 145.563, 154.045, 154.995, 166.626.

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