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Synthesis of 2,5-di(2-thienyl)-1*H*-pyrrole N-linked with conjugated bridges

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Abstract—The Knorr–Paal reaction of 1,4-di(2-thienyl)-1,4-butanedione with anilines to yield *N*-substituted-2,5-di-(2-thienyl)-1*H*-pyrroles (SNS derivatives) was tested by using different acid catalysts in toluene and acetic acid. Di-SNS derivatives were also synthesized in toluene at reflux in the presence of propionic acid, these mild conditions giving acceptable yields in a one-step procedure.

1. Introduction

Over the past 15 years, there has been growing interest in the design and synthesis of new electrically conductive polymers. These quasi one-dimensional polymer systems present attractive electrical and optical properties making them applicable to electronic[1] and photonic devices such as field-effect transistors[2,3] and light-emitting diodes.[4–11] Efforts have been focused on obtaining highly ordered systems, because structural homogeneity and solid-state packing play important roles in determining the properties of conductive polymers.[12–18] Recently, a new concept for the optimisation of three-dimensional solid-state statistical structures of conductive polymers has been presented.[19–26]

We have decided to explore this field by using 2,5-di(2-thienyl)-1*H*-pyrrole derivatives (SNS), for the preparation of conductive polymers cross-linked with different bridges. Ferraris and Skiles[27] first proposed the use of poly-SNS in 1987 as a route to well-defined copolymers that are not easily achieved through oxidative copolymerization of monomer mixtures, even if the monomer oxidation potentials are very similar. SNS derivatives were chosen as polymer precursors for several reasons: (i) the functionalization of the ter-heteroatom unit by use of the Knorr–Paal reaction seemed an attractive one-step procedure for introducing various bridges into the monomer, (ii) the oxidation potential of the SNS derivatives is lower (about +0.7 V vs SCE) than that of their ter-thiophene analogues (about +0.95 V vs SCE),[27,28] and (iii) good quality films of poly-SNS can easily be generated on platinum from various solvents.[29,30] Recently, we proposed the use of dipyrrolyl monomers in which two pyrroles were separated by conjugated spacers.[31] The efficiency of such spacers (phenyl ring derivatives) was limited by their steric hindrance, the phenyl rings being no longer conjugated with the pyrrole moieties in the constrained polymer backbone. By using here *N*,*N*′-di-substituted SNS derivatives, we aimed at obtaining less sterically and geometrically constrained structures, thanks to the intercalation of a bithiophene unit every two *N*-substituted pyrroles in the resulting polymer. Moreover, we planned to synthesize similar SNS derivatives, but with the position 5 blocked. Such molecules, which cannot polymerize, are useful for electrochemical studies on the monomer in the early stage of oxidation. We chose to synthesize these *N*,*N*′-di-substituted SNS derivatives by using a modified double Knorr–Paal reaction[32] involving either 1,4-di(2-thienyl)-1,4-butanedione or 1,4-di(5-methyl-2-thienyl)-1,4-butanedione and various aromatic amines. As will be shown, this condensation reaction is not as trivial as anticipated, especially when diamines are involved. In the present work, full details on the different procedures tested in order to optimise the yields are reported and discussed.

2. Results and discussion

Among the various methods leading to 1,4-di(2-thienyl)-1,4-butanedione,[33–40] the double Friedel–Crafts reaction, first proposed by Merz and Ellinger,[39] was chosen with thiophene and succinyl chloride as the reactants and aluminium chloride as the Lewis acid catalyst, since it is the most direct (one-step procedure with good yields). However, we found that the reaction time can be considerably reduced, the reaction mixture being refluxed for two hours (instead of 24 h stirring at ambient temperature) without loss of yield (50%). It must be noted that the double Friedel–Crafts reaction proceeds with much lower yields when 2-methylthiophene,

Keywords: pyrrole; thiophene; heterocycles; Knorr–Paal reaction.

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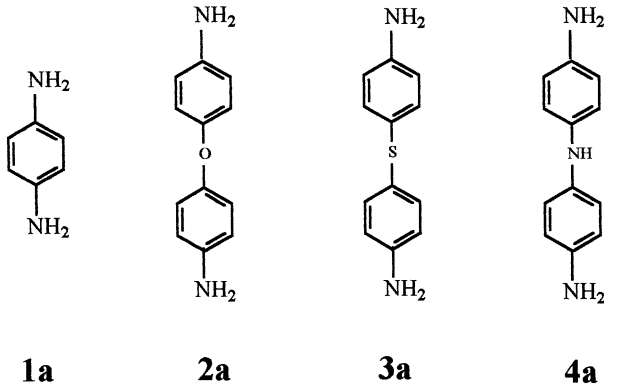


Scheme 1. Structure of the di-amines used for the di-SNS derivative syntheses.

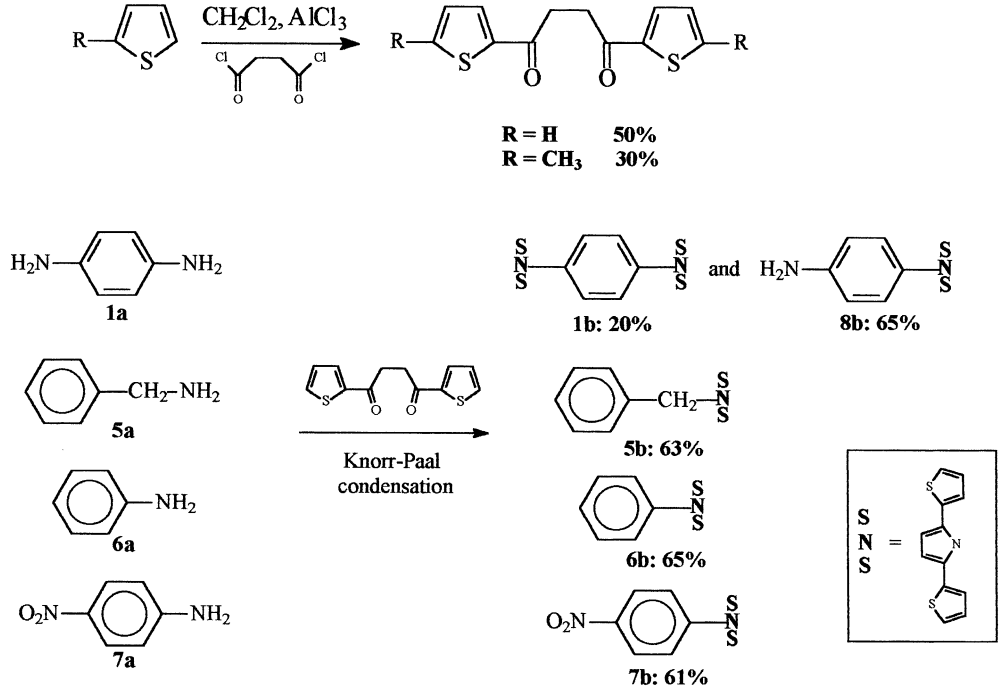
3-methylthiophene or 3-hexylthiophene is used: 30, 20 and 10%, respectively. Moreover, 3-alkylthiophenes lead to mixtures of isomers (this reaction being not selective toward the reactive positions of the thiophene ring). The three isomers, 1,4-di(3-methyl-2-thienyl)-1,4-butanedione, 1-(3-methyl-2-thienyl)-4-(4′-methyl-2′-thienyl)-1,4-butanedione, and 1,4-di(4-methyl-2-thienyl)-1,4-butanedione are separable only by laborious successive recrystallizations from acetonitrile and diethyl ether. In the case of the hexyl derivative, separation of the isomers by recrystallization or chromatography proved impossible. 3-Substituted thiophene rings were used with a view to obtaining more soluble monomers but, owing to the difficulties of purification, we have pursued our investigations only with 1,4-di(2-thienyl)-1,4-butanedione and 1,4-di(5-methyl-2-thienyl)-1,4-butanedione.

Syntheses of various *N*-substituted-2,5-di-(2-thienyl)-1*H*-pyrroles by using the Knorr–Paal reaction with different amines and 1,4-di(2-thienyl)-1,4-butanedione have been reported. This reaction is acid-catalysed (activation of the ketone functions) but the acidity of the medium must be adjusted in order to avoid total protonation of the amine function. This is why the literature indicates various reaction conditions involving different media: benzene or toluene with propionic acid,[41,42] benzene with glacial acetic acid,[27,39,43] benzene and *p*-toluenesulfonic acid (PTSA)[44] or toluene in the presence of titanium tetrachloride as co-operative Lewis acid.[45] The need for a variety of conditions can be explained by the pK_a and the nature of the amine itself (aliphatic, more or less conjugated aromatic), acetic or propionic acid (pK_a in water near 4.8) being generally employed when aliphatic amines are involved whereas *p*-toluenesulfonic acid (pK_a in water <0) is generally preferred in the case of aromatic amines. Only titanium chloride has been used with relative success (yields between 50 and 70%) for both aliphatic and aromatic amines.[45]

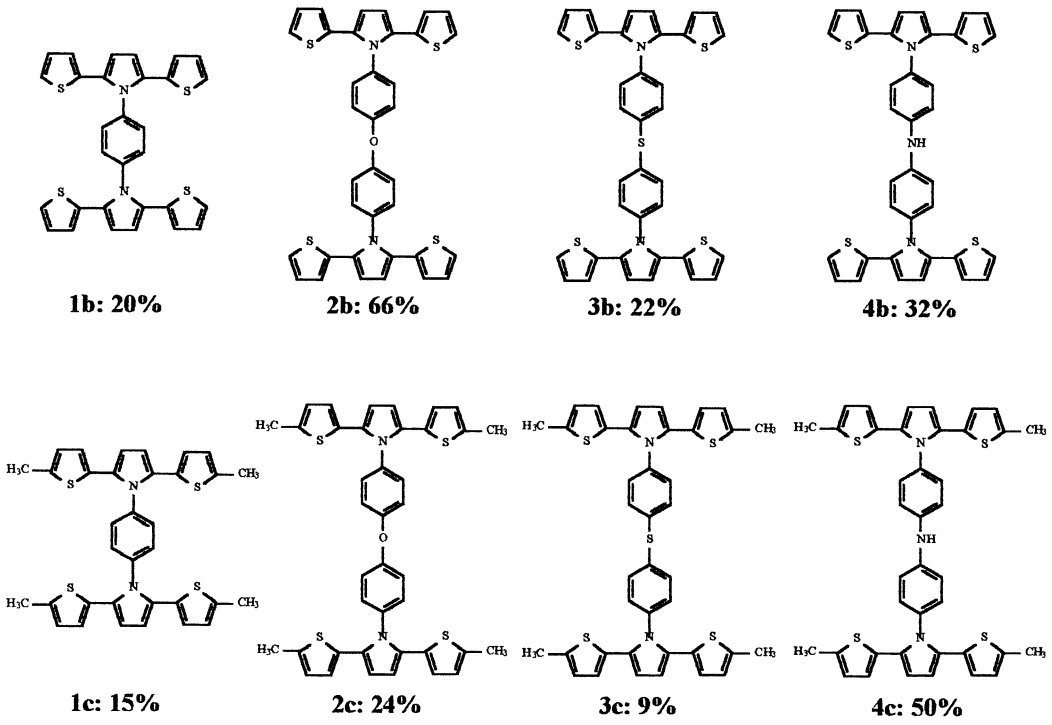
Table 1. Yield of compounds **1b**, **5b**–**7b** by cyclization reactions by procedures A–D (a: not tested)

	1b	**5b**	**6b**	**7b**
Procedure A	8%	63%	17%	0%
Procedure B	0%	47%	65%	61%
Procedure C	20%	48%	40%	a
Procedure D	5%	55%	20%	a

In the present work, the aim was first to perform a double cyclization by the reaction of the two amine functions of the following molecules (Scheme 1): 1,4-benzenediamine (**1a**), 4-(4-aminophenoxy)aniline (**2a**), 4-[(4-aminophenyl)sulfanyl]aniline (**3a**) and *N*1-(4-aminophenyl)-1,4-benzenediamine (**4a**). In order to test the versatility of the cyclization reaction, we first studied di-amine **1a** as well as the following mono-amines: benzylamine (**5a**), aniline



Scheme 2. General route to SNS derivatives, with optimised yields indicated.



Scheme 3. Structures and yields (improved procedure A) of the di-SNS.

(**6a**) and *p*-nitroaniline (**7a**), by using the four procedures A–D given in Section 3. Compounds **5a**, **6a** and **7a** were examined to see how the cyclization reaction responded to the nucleophilicity of the amine. The reaction time in procedures A–D was fixed at 24 h; this parameter might be adapted thereafter. The yields of the desired products **1b**, **5b**, **6b** and **7b** (Scheme 2) relative to the starting butanedione are given in Table 1. In the mono-amine series, the benzylamine **5b** is isolated with similar yields (47–63%) regardless of the method chosen. In the aniline series, the reactivities of **6a** and **7a** are sensitive to the acidity of the reaction medium. This is seen in toluene where *p*-toluenesulfonic acid (procedure B) activates the carbonyl function better than propionic acid (procedure A): in the latter case, no desired compound is obtained from the reaction of the butanedione and *p*-nitroaniline, but only the starting materials with some degradation products. Compared to the parent molecules **5b**–**7b**, the di-SNS derivative **1b** is always obtained in lower yields. This explains the difficulty of accomplishing the second cyclization, as proven by the non-negligible quantities of the mono-reacted product, 4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]aniline **8b**, isolated among the by-products (especially in acetic acid medium). The presence or absence of water is also a critical parameter for the double cyclisation. Indeed, when a Dean–Stark apparatus is used, it is found that another by-product, *N*1-4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]phenylpropanamide **9b**, is formed in significant amounts. For example, when 22 mmol of 1,4-di(2-thienyl)-1,4-butanedione, 10 mmol of **1a** and 22 mmol of propionic acid are engaged following the procedure A, the recovered products are: target molecule **1b** (only 0.5 mmol), 4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]aniline **8b** (6 mmol), *N*1-{4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]-phenyl}propanamide **9b** (2 mmol) and butanedione (5.5 mmol). In the same way, the attempt of forming **1b** in acetic acid in using the direct reaction of **8b** on 1,4-di(2-thienyl)-1,4-butanedione in the presence of magnesium sulfate leads to *N*1-{4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]-phenyl}acetamide **10b** with 61% yield and **1b** with only 4% yield. On the other hand, **8b** is obtained in good yields (65%) following procedure A, even with the use of a Dean–Stark apparatus. This exemplifies the low reactivity of the molecule **8b** and moreover the high competition of the formation of the amide derivative. The removal of water encourages this competitive reaction and lowers the yield of **1b**. Therefore, contrary to the generally accepted ideas,[46] the presence of water in the reactional medium is preferable for double Knorr–Paal reaction. Acetic acid is not the best solvent. Indeed, when the reaction is followed by TLC (dichloromethane as eluent), the cyclization is seen to proceed very slowly in this medium. Competing acid-catalysed self-condensation reactions involving the already formed ter-heterocycles (SNS derivatives) occur, as attested by the numerous insoluble by-products, and the overall yield falls. Such acidity problems were reported in the case of the synthesis of several 1-benzyl- and 1-alkyl-1*H*-pyrroles via the condensation of the corresponding primary amines with 2,5-dimethoxyfuran.[32] This degradation reaction is particularly annoying in the case of **1b** for which the complete reaction of the two amine functions is very slow, as mentioned earlier. Consequently, we cannot expect any improvement in the yield by prolonging the reaction in acetic acid. For the four molecules, the yield of the reaction increases in a given solvent with the acidity of the medium, reaches a maximum, and then decreases. The position of this maximum depends to the pK_a value of the corresponding amine. Thus, for **6b** (pK_a of aniline=4.69[47]), the higher the acidity is, the greater is the yield (40% in acetic acid with 10% PTSA with respect to butanedione). Compound **5b** (pK_a of benzylamine=9.40[48])

is however isolated in greatest amounts when a weak acid catalyst is used, propionic acid, with only 2 mol per mole of butanedione in toluene. Phenylenediamine has a first pk_a value between the previous two (pK_a^1=6.16[49]). As expected, the maximum yield is obtained for intermediate acidic conditions, i.e. when a strong acid catalyst (PTSA) in used in small proportion (1% with respect to butanedione) in acetic acid.

Not only the target molecules but also their mono-reacted amine intermediates have high molecular weights (536–644 and 320–428, respectively). The intermediates must be solubilised in order to undergo the second cyclization. This is why, given the above remarks concerning acetic acid, we chose to use toluene as the solvent with propionic acid as the catalyst for the synthesis of molecules **1b**–**4b**, as well as for molecules **1c**–**4c** (Scheme 3), and to increase the reflux time in order to improve the yields. It was necessary to reflux for at least five days to obtain the desired molecules in acceptable amounts. Under these conditions (procedure A and 5 days reflux) compounds **1b**–**4b** were isolated in 20, 66, 22 and 32% yield, respectively. Their tetramethylated derivatives **1c**–**4c** were also obtained in the same way with yields of 15, 24, 9 and 50%, respectively. It is noticeable that these compounds are obtained in lower yields than the non-methylated parents, except **4c** which is isolated in surprisingly high yield.

3. Experimental

3.1. General methods

Air-sensitive reagents were manipulated in an argon atmosphere. All solvents were dried and purified by standard procedures. ^{1}H NMR spectra were recorded on a Bruker AC 200 (200 MHz) spectrometer in $CDCl_3$ or DMSO-d_6, and chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard, and coupling constants (J) in Hz. GC/MS analyses were performed on an Intersmat IGC 121 FL/ ITD 800 Finnigan MAT spectrometer using a CP-Sil 5 CB low-bleed column and chemical ionisation (CI-isobutane as carrier gas). ESI mass spectra (positive ion mode) and collision-induced decomposition (CID) spectra of selected ions, under low energy conditions, were performed in a triple quadrupole tandem mass spectrometer (Quattro, Micromas).

3.2. Synthesis

3.2.1. 1,4-Di(2-thienyl)-1,4-butanedione. Yield: 53%; white solid; mp 132°C (lit.[32] 130–131°C); calcd for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 4.03; O, 12.78; S, 25.62. Found: C, 57.0; H, 3.8; O, 12.7; S, 25.8%; λ_{max} (CH_3CN)/nm: 259 (ε/mol^{-1} cm^{-1} l^{-1}: 17,900) and 283 (14,700); δ_H ($CDCl_3$): 3.41 (4H, s, $COCH_2$), 7.16 (2H, J=3.8, 1.1 Hz, 4,4′-thienyl), 7.66 (2H, J=3.8, 5.0 Hz, 3,3′-thienyl), 7.83 (2H, J=1.1, 5.0 Hz, 5,5′-thienyl); m/z (CI): 251 (MH^+, 91), 167 (100), 139 (3.6), 111 (10.9) and 79 (7.3).

3.2.2. 1,4-Di(5-methyl-2-thienyl)-1,4-butanedione. Yield 30%; white crystalline solid; mp 176°C; calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07; O, 11.49; S, 23.04. Found: C, 60.2; H, 4.9; O, 11.4; S, 22.6%; λ_{max} (CH_3CN)/nm 268 (ε/dm^3 mol^{-1} cm^{-1} 17,200) and 294 (23,400); δ_H ($CDCl_3$) 2.54 (6H, s, CH_3), 3.32 (4H, s, $COCH_2$), 6.81 (2H, J=3.8 Hz, 3,3′-thienyl), 7.63 (2H, J=3.8 Hz, 4,4′-thienyl); m/z (CI): 279 (MH^+, 36.4), 181 (100), 125 (4.5).

3.3. General procedures for Knorr–Paal reactions

The double Knorr–Paal reaction was studied, especially for the synthesis of compound **1b**, by using the four procedures described below:

Procedure A. A round-bottomed flask equipped with an argon inlet and mechanical stirrer was charged with 1.25 g (5 mmol) of the 1,4-di(2-thienyl)-1,4-butanedione, 2 mmol of the corresponding diamine, 0.4 cm^3 (5.4 mmol) of propionic acid and 15 cm^3 of toluene. The mixture was stirred and refluxed for 24 h under argon. Evaporation of the toluene, followed by chromatography (SiO_2 column, elution with dichloromethane) gave the desired di-ter-heterocycle compound eluting at the solvent front.

The three other procedures are minor modification of procedure A.

Procedure B. 80 mg (0.46 mmol) of PTSA as catalyst instead of propionic acid.

Procedure C. 80 mg (0.46 mmol) of PTSA and 15 cm^3 of glacial acetic acid instead of propionic acid and toluene.

Procedure D. Only glacial acetic acid (15 cm^3), and no acid catalyst was used.

For comparison, the simple Knorr–Paal reaction leading to molecules **5b**–**7b** was monitored by using the same procedures A–D with an equimolecular amount of butanedione and amine (i.e. 2 mmol). The proportions of the acid catalyst relative to the diketone were identical to those given above.

The di-SNS derivatives described below were synthesized by using the improved procedure A (5 days reflux instead of 24 h). They were all purified by column chromatography (dichloromethane as eluent). It was not possible to purify them by recrystallization because of the small quantities obtained and the sensitivities of these products to oxidation in hot solvents. For this reason, chemical analyses were not always as accurate as desired. Nevertheless, the products were completely identified by other techniques, notably ^{1}H NMR and mass spectrometry.

3.3.1. 1-4-Di[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]benzene, 1b. Yield 20% (214 mg); grey powder; mp 302°C; calcd for $C_{30}H_{20}N_2S_4$: C, 67.16; H, 3.73; N, 5.22; S, 23.88. Found: C, 69.0; H, 4.9; N, 4.5; S, 22.3%; λ_{max} (CH_3CN)/nm 238 (ε/dm^3 mol^{-1} cm^{-1} 11,200) and 323 (10,100); δ_H (DMSO-d_6) 6.57 (4H, s, pyrrolyl), 6.72 (4H, J=3.6, 1.1 Hz, 3-thienyl), 6.96 (4H, J=3.6, 5.1 Hz, 4-thienyl), 7.44 (4H, J=1.1, 5.1 Hz, 5-thienyl), 7.46 (4H, s, phenyl).

3.3.2. 1-4-Di[2,5-di(5-methyl-2-thienyl)-1*H*-1-pyrrolyl]-benzene, 1c. Yield 15% (177 mg); pale red powder; mp 227°C; calcd for $C_{34}H_{28}N_2S_4$: C, 68.91; H, 4.72; N, 4.72;

S, 21.62. Found: C, 69.2; H, 6.3; N, 4.0; S, 18.7%; λ_{max} (CH_3CN)/nm 241 (ε/dm^3 mol^{-1} cm^{-1} 9800) and 323 (10,400); δ_H ($CDCl_3$) 2.42 (12H, s, CH_3), 6.29 (4H, *J*=3.5 Hz, 3-thienyl), 6.45 (4H, s, pyrrolyl), 6.49 (4H, *J*=3.5 Hz, 4-thienyl), 7.32 (4H, s, phenyl); *m*/*z* (CI): 593 (MH^+, 100), 574 (12.1) and 475 (7.5).

3.3.3. Di{4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]phenyl}ether, 2b. Yield 66% (829 mg); brown powder; mp 250°C; calcd for $C_{36}H_{24}N_2S_4O$: C, 68.79; H, 3.82; N, 4.45; O, 2.55; S, 20.38. Found: C, 68.9; H, 4.1; N, 4.4; O, 2.7; S, 20.0%; λ_{max} (CH_3CN)/nm 238 (ε/dm^3 mol^{-1} cm^{-1} 11,400) and 334 (11,300); δ_H ($CDCl_3$) 6.56 (4H, s, pyrrolyl), 6.65 (4H, *J*=3.6, 1.1 Hz, 3-thienyl), 6.87 (4H, *J*=3.6, 5.1 Hz, H 4-thienyl), 7.09 (4H, *J*=1.1, 5.1 Hz, 5-thienyl), 7.12 (4H, *J*=8.7, 2.2 Hz, phenyl), 7.33 (4H, *J*=8.7, 2.2 Hz, phenyl).

3.3.4. Di{4-[2,5-di(5-methyl-2-thienyl)-1*H*-1-pyrrolyl]-phenyl}ether, 2c. Yield 24% (328 mg); brown powder; mp 182°C; calcd for $C_{40}H_{32}N_2S_4O$: C, 70.17; H, 4.68; N, 4.09; O, 2.34; S, 18.71. Found: C, 70.0; H, 5.0; N, 4.0; O, 2.6; S, 18.4%; λ_{max} (CH_3CN)/nm 241 (ε/dm^3 mol^{-1} cm^{-1} 10,900) and 331 (11,000); δ_H ($CDCl_3$) 2.38 (12H, s, CH_3), 6.39 (4H, *J*=3.6 Hz, 3-thienyl), 6.46 (4H, s, pyrrolyl), 6.50 (4H, m, 4-thienyl), 7.11 (4H, *J*=8.8 Hz, phenyl), 7.31 (4H, *J*=8.8 Hz, phenyl); *m*/*z* (CI): 685 (MH^+, 57.2), 567 (22.0), 310 (100) and 293 (65.9).

3.3.5. Di{4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]phenyl}sulfide, 3b. Yield 22% (283 mg); pink powder; mp 245°C; calcd for $C_{36}H_{24}N_2S_5$: C, 67.08; H, 3.73; N, 4.35; S, 24.84. Found: C, 68.9; H, 4.9; N, 4.0; S, 22.3%; λ_{max} (CH_3CN)/nm 251 (ε/dm^3 mol^{-1} cm^{-1} 15,800) and 326 (14,400); δ_H ($CDCl_3$) 6.54 (4H, s, pyrrolyl), 6.60 (4H, *J*=3.6, 1.1 Hz, 3-thienyl), 6.84 (4H, *J*=3.6, 5.1 Hz, 4-thienyl), 7.08 (4H, *J*=1.1, 5.1 Hz, 5-thienyl), 7.27 (4H, *J*=8.6, 2.1 Hz, p henyl), 7.39 (4H, *J*=8.6, 2.1 Hz, phenyl).

3.3.6. Di{4-[2,5-di(5-methyl-2-thienyl)-1*H*-1-pyrrolyl]-phenyl}sulfide, 3c. Yield 9% (126 mg); pale brown powder; mp 185°C; calcd for $C_{40}H_{32}N_2S_5$: C, 68.57; H, 4.57; N, 4.00; S, 22.86. Found: C, 68.6; H, 4.9; N, 3.9; S, 22.6%); λ_{max} (CH_3CN)/nm 255 (ε/dm^3 mol^{-1} cm^{-1} 14,900) and 325 (14,200); δ_H ($CDCl_3$) 2.53 (12H, s, CH_3), 6.34 (4H, *J*=3.5 Hz, 3-thienyl), 6.45 (4H, s, pyrrolyl), 6.47 (4H, *J*=3.5 Hz, 4-thienyl), 7.26 (4H, *J*=8.2 Hz, phenyl), 7.40 (4H, *J*=8.2 Hz, phenyl).

3.3.7. *N*,*N*-Di{4-[2,5-di(2-thienyl)-1*H*-1-pyrrolyl]phenyl}-amine, 4b. Yield 32% (401 mg); brown powder; mp 257°C; calcd for $C_{36}H_{25}N_3S_4$: C, 68.90; H, 3.99; N, 6.70; S, 20.41; Found: C, 70.6; H, 4.7; N, 6.1; S, 18.5%); λ_{max} (CH_3CN)/nm 237 (ε/dm^3 mol^{-1} cm^{-1} 9500), 312 (13,100) and 342 (7000); δ_H ($CDCl_3$) 6.55 (4H, s, pyrrolyl), 6.68 (4H, *J*=3.6, 1.1 Hz, 3-thienyl), 6.86 (4H, *J*=3.6, 5.1 Hz, 4-thienyl), 7.08 (4H, *J*=1.1, 5.1 Hz, 5-thienyl), 7.17 (4H, *J*=9.0, 2.5 Hz, phenyl), 7.33 (4H, *J*=9.0, 2.5 Hz, phenyl).

3.3.8. *N*,*N*-Di{4-[2,5-di(5-methyl-2-thienyl)-1*H*-1-pyrrolyl]phenyl}amine, 4c. Yield 50% (683 mg); brown powder; mp 202°C; calcd for $C_{40}H_{33}N_3S_4$: C, 70.27; H, 4.83; N, 6.15; S, 18.74; Found: C, 70.9; H, 5.2; N, 5.8; S, 18.0%); λ_{max} (CH_3CN)/nm 242 (ε/dm^3 mol^{-1} cm^{-1} 9300), 313 (12,800) and 340 (7200); δ_H ($CDCl_3$) 2.40 (12H, s, CH_3), 6.41 (4H, *J*=3.5 Hz, 3-thienyl), 6.46 (4H, s, pyrrolyl), 6.51 (4H, *J*=3.5 Hz, 4-thienyl), 7.16 (4H, *J*=9.0 Hz, phenyl), 7.24 (4H, *J*=9.0 Hz, phenyl); *m*/*z* (CI): 684 (MH^+, 84.8), 566 (9.1), 391 (100) and 293 (43.2).

3.3.9. 1-Benzyl-2,5-di(2-thienyl)-1*H*-pyrrole, 5b. Via procedure B. Yield 47% (300 mg); pale brown powder; mp 99°C; calcd for $C_{19}H_{15}NS_2$: C, 71.03; H, 4.67; N, 4.36; S, 19.94; Found: C, 70.5; H, 5.0; N, 4.2; S, 19.3%; λ_{max} (CH_3CN)/nm 231 (ε/dm^3 mol^{-1} cm^{-1} 10,100) and 317 (13,600); δ_H ($CDCl_3$) 5.39 (2H, s, CH_2), 6.49 (2H, s, pyrrolyl), 6.81 (2H, *J*=1.1, 3.6 Hz, 3-thienyl), 6.94 (2H, *J*=3.6, 5.1 Hz, 4-thienyl), 6.97 (2H, m, phenyl), 7.21 (2H, *J*=1.1, 5.1 Hz, 5-thienyl), 7.31 (3H, m, phenyl); *m*/*z* (CI): 322 (MH^+, 100).

3.3.10. 1-Phenyl-2,5-di(2-thienyl)-1*H*-pyrrole, 6b. Via procedure B. Yield 65% (400 mg); brown–green powder; mp 180°C; calcd for $C_{18}H_{13}NS_2$: C, 70.36; H, 4.23; N, 4.56; S, 20.85. Found: C, 70.5; H, 4.2; N, 4.5; S, 20.9%); λ_{max} (CH_3CN)/nm 240 (ε/dm^3 mol^{-1} cm^{-1} 14,900) and 331 (22,400); δ_H ($CDCl_3$) 6.53 (2H, *J*=1.0, 3.6 Hz, 3-thienyl), 6.56 (2H, s, pyrrolyl), 6.82 (2H, *J*=3.6, 5.1 Hz, 4-thienyl), 7.07 (2H, *J*=1.0, 5.1 Hz, 5-thienyl), 7.33 (2H, m, *J*=7.7, 2.0 Hz, phenyl), 7.44 (3H, m, phenyl); *m*/*z* (CI): 308 (MH^+, 100).

3.3.11. 1-(4-Nitrophenyl)-2,5-di(2-thienyl)-1*H*-pyrrole, 7b. Via procedure B. Yield 61% (429 mg); pale orange crystals; mp 215°C; calcd for $C_{18}H_{12}N_2O_2S_2$: C, 61.36; H, 3.41; N, 7.95; O, 9.09; S, 18.18; Found: C, 61.3; H, 3.5; N, 8.0; O, 9.1; S, 18.3%; λ_{max} (CH_3CN)/nm 233 (ε/dm^3 mol^{-1} cm^{-1} 15,500) and 319 (15,000); δ_H ($CDCl_3$) 6.55 (2H, *J*=1.1, 3.6 Hz, 3-thienyl), 6.56 (2H, s, pyrrolyl), 6.87 (2H, *J*=3.6, 5.1 Hz, 4-thienyl), 7.15 (2H, *J*=1.1, 5.1 Hz, 5-thienyl), 7.41 (2H, *J*=9.0, 2.1 Hz, phenyl), 8.23 (2H, *J*=9.0, 2.1 Hz, phenyl); *m*/*z* (CI): 353 (M^+, 100), 336 (7.4) and 306 (4.2).

3.3.12. 4-[2,5-Di(2-thienyl)-1*H*-1-pyrrolyl]aniline, 8b. Via procedure A. Yield 65%; grey powder; mp 189°C; calcd for $C_{18}H_{14}N_2S_2$: C, 67.08; H, 4.35; N, 8.69; S, 19.87; Found: C, 67.7; H, 4.8; N, 8.3; S, 19.3%; δ_H ($CDCl_3$) 3.87 (2H, NH_2), 6.53 (2H, s, pyrrolyl), 6.64 (2H, *J*=3.65, 1.15 Hz, 3-thienyl), 6.84 (2H, *J*=3.65, 5.10 Hz, 4-thienyl), 7.05 (2H, *J*=1.15, 5.10 Hz, 5-thienyl), 6.72 (2H, *J*=6.58, 2.15 Hz, phenyl), 7.10 (2H, *J*=6.58, 2.15 Hz, phenyl).

3.3.13. *N*1-{4-[2,5-Di(2-thienyl)-1*H*-1-pyrrolyl]phenyl}-propanamide, 9b. Greenish grey powder, δ_H ($CDCl_3$) 1.28 (3H, *J*=7.5 Hz, CH_3), 2.44 (2H, *J*=7.5 Hz, CH_2), 6.57 (2H, *J*=3.65, 1.15 Hz, 3-thienyl), 6.53 (2H, s, pyrrolyl), 6.82 (2H, *J*=3.65, 5.13 Hz, 4-thienyl), 7.05 (2H, *J*=1.15, 5.13 Hz, 5-thienyl), 7.26 (2H, *J*=8.7 Hz, phenyl), 7.60 (2H, *J*=8.7 Hz, phenyl).

3.3.14. *N*1-{4-[2,5-Di(2-thienyl)-1*H*-1-pyrrolyl]phenyl}acetamide, 10b. Greenish grey powder, δ_H ($CDCl_3$) 2.23 (3H, CH_3), 6.57 (2H, *J*=3.65, 1.15 Hz, 3-thienyl), 6.53 (2H, s, pyrrolyl), 6.82 (2H, *J*=3.65, 5.13 Hz, 4-thienyl),

7.05 (2H, J=1.15, 5.13 Hz, 5-thienyl), 7.26 (2H, J=8.7 Hz, phenyl), 7.60 (2H, J=8.7 Hz, phenyl).

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