

Thienylpyrrole azo dyes: synthesis, solvatochromic and electrochemical properties

M. Manuela M. Raposo,^{a*} Ana M. R. C. Sousa,^a A. Maurício C. Fonseca^a
and G. Kirsch^b

^a Centro de Química, Universidade do Minho, Campus de Gualtar
4710-057 Braga, Portugal

^b Laboratoire d'Ingénierie Moléculaire et Biochimie Pharmacologique,
UFR SciFA/Université de Metz, 1, Boulevard Arago, Metz Technopôle,
57078 Metz Cedex 3, France

Abstract – The synthesis and the evaluation of solvatochromic and electrochemical properties of new donor-acceptor-substituted thienylpyrrole azo dyes **3** are described. These derivatives exhibit dramatic changes in both their electronic and redox properties in comparison with thienylpyrroles **1**. In agreement with the solvatochromic and electrochemical studies of push-pull derivatives **3** the new compounds prepared, may find application in the manufacture of new materials with notable non-linear optical properties.

Keywords: donor-acceptor thienylpyrroles, azo dyes, UV-visible spectroscopy, chromophores, solvatochromism, electrochemistry, nonlinear optics (NLO).

1. Introduction

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials have attracted much attention in recent years.¹⁻² They have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.³ Organic NLO materials have many advantages over inorganic materials, including large nonlinear optical coefficients, greater ease of synthetic design, easy preparation and lower cost.⁴⁻⁵ It has been shown that the second order hyperpolarizabilities (β) of heterocyclic chromophores are often higher than their benzene analogues.⁶⁻⁷ Recently we have also demonstrated that donor-acceptor

*Corresponding author. Phone: +351 253 604381; Fax: +351 253 678983; e-mail: mfox@quimica.uminho.pt

substituted bithiophenes and terthiophenes have many favorable features as NLO materials.⁸⁻¹¹

Use of conjugated thiophene and pyrrole derivatives as donors combined with substituted acceptor groups are promising candidates among such D-A systems due to their numerous applications. Unlike the thiophene or furan analogues, the pyrrole ring can be further substituted at the nitrogen atom so that the electron density of the chromophore can be changed. In addition, replacing the N-H group of the pyrrole ring with another substituent would eliminate some intramolecular hydrogen bondings which might also affect their macroscopic structures and NLO properties.¹²⁻²¹

Azo dyes with heterocyclic diazo components have been intensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics. These results led to the development of commercial products which replaced the conventional azobenzene disperse dyes.²²

A renewed interest in aryl(heteroaryl)-azo dyes has been sparked by efforts to find organic second-order non-linear optical (NLO) materials suitable for applications such as harmonic generation and optical switching. Azo dyes are of particular interest because they can be readily prepared with a wide range of donor and acceptor groups and also because the planarity of the azo bridge *versus* the nonplanarity of stilbenes or other systems should contribute to larger π electron transmission effects and lead to higher optical activity.²²⁻²⁵

These previous studies prompted us to the synthesis and the characterization of new thienylpyrrole azo dyes as suitable candidates for potential use in optical data storage devices.

As part of our continuing interest in non-linear optical material^{8-11,26-27} we report in this paper the synthesis, the solvatochromic and the electrochemical properties of new 1-alkyl(aryl)-2-(2'-thienyl)-5-phenylazopyrrole derivatives **3** which have *para* CO₂Me, CN, NO₂ and *ortho-para* NO₂ groups as the electron-withdrawing groups on the phenylazo moiety and the conjugated 1-alkyl(aryl)-2-(2'-thienyl)pyrrole, as strong π -electron donor moieties.

2. Results and discussion

2.1. Synthesis

Recently we have reported the synthesis of thienylpyrroles **1** through a combination of Friedel-Crafts and Lawesson reactions.²⁸ Compounds **1** have proved to be versatile substrates in diazo coupling reactions, allowing the preparation of several new donor-acceptor substituted thienylpyrroles.

The synthesis of thienylpyrrole azo dyes **3** is outlined in Scheme 1. The coupling reaction of aryldiazonium salts **2a-d**, with 1-alkyl(aryl)-2-(2'-thienyl)pyrroles **1A-H** gave rise to the formation of 1-alkyl(aryl)-2-(2'-thienyl)-5-phenylazopyrrole derivatives **3**. This functionalization was made by reacting 1-alkyl(aryl)-2-(2'-thienyl)pyrroles **1A-H** with aryldiazonium salts **2a-d** in acetonitrile/acetic acid for 2h at 0 °C.

Diazo coupling was accomplished selectively at the 5-position²⁹⁻³⁰ of pyrrole ring to give compounds **3** in moderate to excellent yields (31-90%), (Scheme 1, Table 1). These results are in accordance with the greater nucleophilicity of the pyrrole ring *versus* the thiophene ring as has been shown earlier in the case of formylation and tricyanovinylolation of thienylpyrroles.³¹⁻³⁴

The structures of the thienylpyrrole azo dyes **3** were unambiguously confirmed by their analytical and spectral data.

<SCHEME 1>

<TABLE 1>

2.2. UV-visible and solvatochromic studies of thienylpyrrole azo dyes

Electronic absorption spectra of compounds **3** show an intense lowest energy charge-transfer absorption band in the UV-visible region. Dramatic differences in energy occur upon arylazo substitution of thienylpyrroles **1**. For example, 1-aryl-2-(2'-thienyl)pyrrole **1D** ($\lambda_{\max} = 290.0$ nm) is shifted 241.0 nm upon arylazo substitution

(thienylpyrrole azo dye **3Dd**, $\lambda_{\max} = 531.0$ nm) (Table 1). The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of compounds **3Da** and **3Dd** as the longest wavelength transition is shifted from 473.0 nm in 1-(4''-methoxyphenyl)-2-(2'-thienyl)-5-(4'''-carbomethoxyphenylazo)pyrrole **3Da** (Table 1, entry 1) to 531.0 nm for 1-(4''-methoxyphenyl)-2-(2'-thienyl)-5-(2''',4'''-dinitrophenylazo)pyrrole **3Dd** (Table 1, entry 11). This effect has been attributed to the stabilization of LUMO by the electron-withdrawing groups.³⁵ A distinct spectral effect is also caused by the substituent at the nitrogen atom of the pyrrole ring. The influence of the substituent on the nitrogen atom of the pyrrole ring is demonstrated by comparison of the absorption maxima of compounds **3Ac** and **3Ec** as the longest wavelength transition is shifted from 488.0 nm in 1-(*n*-propyl)-2-(2'-thienyl)-5-(4''-nitrophenylazo)pyrrole **3Ac** (Table 1, entry 3) to 507.0 nm for 1-(2'',4''-dimethoxyphenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole **3Ec** (Table 1, entry 7).

To evaluate the intermolecular forces between solvents and solute molecules and in order to determine the best indicator dye, we carried out a preliminary study of the absorption spectra for compounds **3** in selected solvents of different solvation character (diethyl ether, ethanol and DMF). We found that compound **3Dc** shows the greatest shift in wavenumber maxima ($\Delta\nu_{\max} = 801$ cm⁻¹). Therefore, **3Dc** was submitted to a full solvatochromic study involving 15 solvents (Table 2). With respect to the influence of the solvent on the absorption properties of the compounds studied, a bathochromic shift of the longest wavelength bands is generally observed as a result of an increase in the solvent polarity (positive solvatochromism; $\Delta\nu = +2088$ cm⁻¹ for **3Dc**). Because of its pronounced solvatochromism, good correlation with π^* values by Kamlet and Taft³⁶⁻³⁷ for the solvents investigated and long wavelength absorption in the visible range, **3Dc** seemed to be a very appropriate solvent polarity indicating dye (Table 2).

<TABLE 2>

Color chemistry studies have demonstrated that the replacement of a benzene ring by a less aromatic heterocycle in typical donor-acceptor chromogens, such as azo and

stilbene dyes, results in a significant bathochromic shift of the visible absorption spectra. This red shift, obtained for example with thiophene, furan, pyrrole and thiazole rings suggests an increase of molecular hyperpolarizability, accordingly to theoretical NLO studies. Experimental data confirmed this positive effect, in particular, for thiophene ring. In accordance with other solvatochromic studies for heteroaryl-azo dyes, the increase of the electron-withdrawing strength on the substituent of the diazo component and/or the increase of the electron-donating strength of the coupling moiety was found to cause pronounced bathochromism. In general, red shifts in absorption were accompanied by positive solvatochromic shifts.³⁹⁻⁴⁶

2.3. Electrochemistry of thienylpyrrole precursors **1** and thienylpyrrole azo dyes **3**

To obtain a deeper insight into the ground state properties and more specifically the mutual donor-acceptor electronic influence, we studied the redox properties of the thienylpyrroles **1** and thienylpyrrole azo dyes **3** by cyclic voltammetry. These results are presented in Table 3.

Upon diazo coupling, the thienylpyrrole azo dyes **3** display oxidations at more positive potentials as a consequence of the destabilizing effect of the electron-withdrawing group on the phenylazo moiety. For example thienylpyrrole azo dye **3Dd** displays an oxidation at $^1E_{pa} = 0.68$ V, an anodic shift of 0.20 V with respect to the unsubstituted thienylpyrrole **1D**.

Compounds **3Da** and **3Db** exhibit three redox processes, two oxidations and one reduction. The pyrroles azo dyes **3Ac-Hc** and **3Dd** exhibit four redox processes, two oxidation and two reductions. In the anodic scan, the first of these processes is associated with the irreversible oxidation of the pyrrole moiety. These results are consistent with previous electrochemical studies of other pyrrole and thiophene derivatives.^{17,47-48} The second anodic feature is assigned to the irreversible oxidation of the azobenzene moiety.⁴⁷

A variation of the peak potential for oxidation of the pyrrole moiety reflect the magnitude of the electronic influence exerted upon the pyrrole ring system by the terminal electron-withdrawing substituent of the azoaryl group, *e.g.* 1-(4''-methoxyphenyl)-2-(2'-thienyl)-5-(4'''-carbomethoxyphenylazo)pyrrole **3Da** display a

first oxidation at ${}^1E_{pa} = 0.57$ V and 1-(4''-methoxyphenyl)-2-(2'-thienyl)-5-(2''',4'''-dinitrophenylazo)pyrrole **3Dd** display an oxidation at ${}^1E_{pa} = 0.68$ V.

Cyclic voltammetry of all the compounds **3** shows a reversible reduction attributed to the azobenzene moieties.⁴⁷ The cathodic regime in the voltammetry of the pyrroles azo dyes, **3Ac-3Hc** and **3Dd**, studied revealed two reversible couples. These correspond to the one electron reduction of the nitro (${}^1E_{1/2}$) and azobenzene moieties (${}^2E_{1/2}$), respectively. Compounds **3Da** and **3Db** shows only one reversible reduction due to the azobenzene moiety.

The extent of the interaction between the electron donating and accepting termini is dependent on the substituent group at the nitrogen atom on the pyrrole ring. For example, 1-(*n*-propyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole **3Ac** display a second reduction at ${}^2E_{1/2} = -1.70$ V and 1-(4''-methoxyphenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole **3Dc** display a reduction at ${}^2E_{1/2} = -1.83$ V.

<FIGURE 1>

In summary, we have achieved the first synthesis of a series of thienylpyrrole azo dyes **3** in moderate to excellent yields. By comparing the several derivatives synthesized, it can be shown that the withdrawing group on the phenylazo moiety and the type of substituent on the nitrogen atom of the pyrrole ring have significant influence on the solvatochromic and electrochemical properties of these compounds. These derivatives exhibit dramatic changes in both their electronic and redox properties in comparison to thienylpyrroles **1**.

The study of the nonlinear optical properties of the new donor-acceptor systems is currently underway.

3. Experimental

3.1. General

¹H NMR spectra were obtained on a Varian Unity Plus Spectrometer at 300 MHz and ¹³C NMR spectra were determined on a Varian Unity Plus Spectrometer at 75.4 MHz using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. UV-visible absorption spectra were obtained using a Shimadzu UV/2501PC spectrophotometer. EI mass spectra EI (70 eV) and HRMS were run on a Unicam GC-MS 120. Elemental analysis was carried out on a Leco CHNS-932. Voltammetric measurements were performed using a potentiostat/galvanostat (AUTOLAB /PSTAT 12) with the low current module ECD from ECO-CHEMIE and the data analysis processed by the General Purpose Electrochemical System software package also from ECO-CHEMIE. Three electrode-two compartment cells equipped with vitreous carbon-disc working electrodes, a platinum-wire secondary electrode and a silver-wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The concentration of the compounds were typically 1-2 mmol dm⁻³ and 0.2 mol dm⁻³ [NBu₄][BF₄] was used as the supporting electrolyte in *N,N*-dimethylformamide solvent. The potential is measured with respect to ferrocinium/ferrocene as an internal standard. Column chromatography was performed on Merck silica gel 60 (Art 9385). Light petroleum refers to solvent boiling in the range 40-60 °C.

4-Nitroaniline, 4-cyanoaniline, 4-carbomethoxyaniline and 2,4-dinitroaniline used as precursors for the synthesis of aryldiazonium salts **2a-d** were purchased from Aldrich and Fluka and used as received.

The synthesis of thienylpyrroles **1A-H** has been described elsewhere.²⁸

3.2. General procedure for diazo coupling of thienylpyrroles 1A-H with 4-carbomethoxy-, 4-cyano- and 4-nitro-substituted aryldiazonium salts 2a-c

i) Diazotisation of 4-carbomethoxy-, 4-cyano- and 4-nitroaniline

Aniline (4.0 mmol) was pasted with NaNO₂ (4.0 mmol) and water (10 ml) to a smooth slurry and it was added to a well-stirred mixture of HCl (d = 1.18; 3 ml) and ice (3 g) at 0 - 5 °C. The reaction mixture was stirred for 30min.

ii) Coupling reaction with thienylpyrroles 1A-H

The diazonium salt solution previously prepared (4.0 mmol) was added drop wise to the solution of thienylpyrroles **1** (4.0 mmol) in acetonitrile (50 ml) and some drops of acetic acid. The combined solution was maintained at 0 °C for 2 h with stirring. After this time the resulting mixture was diluted with petrol ether (20 ml) and water (40 ml) and the product formed was isolated by filtration. The organic layer was diluted with chloroform, washed with water and dried with anhydrous MgSO₄. The dried solution was evaporated and the remaining 1-alkyl(aryl)-2-(2'-thienyl)-5-(phenylazo)pyrroles **3** were purified by column chromatography on silica with increasing amounts of ether in light petroleum as eluent.

3.2.1. 1-(4''-Methoxyphenyl)-2-(2'-thienyl)-5-(4'''-carbomethoxyphenylazo)pyrrole 3Da. Dark gray solid with metallic luster (85%). Mp: 193.8-194.2 °C. Recrystallization from acetone gave a gray solid mp 195.5-197.0 °C. UV (EtOH): λ_{máx} nm (ε /M⁻¹ cm⁻¹) 473.0 (31,700), 260.0 (10,080), 227.0 (19,520). IR (Nujol) ν 1711 (C=O), 1603, 1536, 1512, 1424, 1363, 1326, 1278, 1226, 1191, 1166, 1110, 981, 836, 767, 692, 591 cm⁻¹. ¹H NMR (Acetone-d₆) δ 3.90 (s, 3H, OCH₃), 3.99 (s, 3H, COOMe), 7.14 (m, 3H, 4'-H and 2'' and 6''-H or 3'' and 5''-H), 7.29 (m, 3H, 3-H, 3'' and 5''-H or 2'' and 6''-H), 7.64 (dd, 1H, J=3.9 and 1.2 Hz, 3'-H), 7.69 (dd, 1H, J=5.1 and 1.2 Hz, 5'-H), 7.80 (d, 2H, J=8.7 Hz, 2''' and 6'''-H), 7.99 (d, 2H, J=9.0 Hz, 3''' and 5'''-H), 9.37 (d, 1H, J=5.4 Hz, 4-H). ¹³C NMR (CDCl₃) δ 52.19, 55.76, 115.32, 118.28, 121.61, 123.27, 125.73, 128.82, 128.93, 130.09, 130.13, 130.97, 134.63, 135.86, 145.43, 145.54, 151.10, 161.67, 166.19. MS (EI) m/z (%): 417 (M⁺ 100), 416 (10), 402 (6), 358 (7), 254 (20), 121 (33). Anal. Calcd for C₂₃H₁₉N₃O₃S: C, 66.14; H, 4.55; N, 10.06; S, 7.68. Found: C, 66.30; H, 4.70; N, 10.35; S, 7.85. HRMS: m/z (EI) for C₂₃H₁₉N₃O₃S; calcd 417.1147; found 417.1142.

3.2.2. 1-(4''-Methoxyphenyl)-2-(2'-thienyl)-5-(4'''-cyanophenylazo)pyrrole 3Db.

Dark red solid with metallic luster (84%). Mp: 196.4-197.2 °C. Recrystallization from acetone gave a dark red solid with metallic luster 198.0-199.5 °C. UV (EtOH): λ_{max} nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 479.0 (37,640), 259.0 (11,700), 228.0 (22,200). IR (Nujol) ν 2223 (CN), 1600, 1538, 1496, 1462, 1442, 1426, 1384, 1361, 1326, 1285, 1229, 1192, 1167, 1148, 1107, 1092, 1015, 980, 914, 838, 801, 729, 645, 619, 510 cm^{-1} . ^1H NMR (Acetone- d_6) δ 3.99 (s, 3H, OCH₃), 7.25 (m, 3H, 4'-H, 2'' and 6''-H or 3'' and 5''-H), 7.45 (d, 1H, $J=5.1$ Hz, 3-H), 7.58 (d, 2H, $J=9.0$ Hz, 2'' and 6''-H or 3'' and 5''-H), 7.71 (dd, 1H, $J=3.9$ and 1.2 Hz, 3'-H), 7.78-7.84 (m, 5H, 5'-H, 2''', 3''', 5''' and 6'''-H), 8.27, (br d, 1H, $J=5.1$ Hz, 4-H). ^{13}C NMR (Acetone- d_6) δ 55.94, 104.28, 112.19, 113.76, 115.16, 119.29, 122.80, 128.09, 128.36, 128.63, 129.52, 129.83, 131.47, 131.59, 134.06, 134.06, 134.46, 150.43, 161.37. MS (EI) m/z (%): 384 (M^+ 100), 254 (19), 223 (10), 192 (8), 121 (36), 77 (5). Anal. Calcd for C₂₂H₁₆N₄OS: C, 68.74; H, 4.16; N, 14.58; S, 8.35. Found: C, 68.90; H, 4.05; N, 14.75; S, 8.60. HRMS: m/z (EI) for C₂₂H₁₆N₄OS; calcd 384.1045; found 384.1043.

3.2.3. 1-(*n*-Propyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Ac. Green solid

with metallic luster (63%). Mp: 148.0-149.0 °C. Recrystallization from acetone gave a green solid with metallic luster 150.0-151.0 °C. UV (EtOH): λ_{max} nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 488.0 (25,100), 289.0 (7900), 218.0 sh(11,600). IR (Nujol) ν 1615, 1550, 1488, 1417, 1330, 1283, 1260, 1137, 851, 748, 533, 509 cm^{-1} . ^1H NMR (DMSO- d_6) δ 0.87 (t, 3H, $J=7.2$, CH₂CH₂CH₃), 1.77-1.83 (m, 2H, CH₂CH₂CH₃), 4.50-4.60 (m, 2H, CH₂CH₂CH₃), 6.80 (d, 1H, $J=4.5$ Hz, 3-H), 6.96 (d, 1H, $J=4.5$ Hz, 4-H), 7.24-7.28 (m, 1H, 4'-H), 7.54 (dd, 1H, $J=3.6$ and 1.2 Hz, 3'-H), 7.80 (dd, 1H, $J=5.1$ and 1.2 Hz, 5'-H), 7.94 (d, 2H, $J=9.3$ Hz, 2'' and 6''-H), 8.34 (d, 2H, $J=9.3$ Hz, 3'' and 5''-H). ^{13}C NMR (DMSO- d_6) 10.99, 24.26, 45.18, 103.35, 114.35, 122.13, 125.14, 127.83, 128.38, 128.57, 131.94, 135.38, 146.56, 147.65, 156.87. MS (EI) m/z (%): 340 (M^+ , 100), 203 (98), 179 (65), 162 (70), 121 (58). Anal. Calcd for C₁₇H₁₆N₄O₂S: C, 60.00; H, 4.70; N, 16.47; S, 9.43. Found: C, 60.25; H, 4.85; N, 16.63; S, 9.72. HRMS: m/z (EI) for C₁₇H₁₆N₄O₂S; calcd 340.0994; found: 340.0998.

3.2.4. 1-Phenyl-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Bc. Green solid with metallic luster (70%). Mp: 158.9-159.2 °C. Recrystallization from acetone gave a green

solid with metallic luster 161.0-163.0 °C. UV (EtOH): λ_{\max} nm (ϵ /M⁻¹ cm⁻¹) 497.0 (33,480), 297.0 (9400), 257.0 (9140), 230.0 (17,820). IR (Nujol) ν 1583, 1513, 1455, 1379, 1350, 1333, 1318, 1239, 1226, 1193, 1147, 1102, 1040, 914, 887, 859, 848, 766, 753, 721, 693, 642, 593, 573, 506 cm⁻¹. ¹H NMR (DMSO-d₆) δ 7.00-7.05 (m, 1H, 4'-H), 7.06-7.10 (m, 2H, 3-H and 4''-H), 7.16 (dd, 1H, J =3.8 and 1.2 Hz, 3'-H), 7.49-7.64 (m, 8H, 4-H, 5'-H, 2'', 3'', 5'', 6'' and 2''', 6'''-H), 8.25 (d, 2H, J =9.0 Hz, 3''' and 5'''-H). ¹³C NMR (DMSO-d₆) 103.14, 113.05, 121.50, 125.04, 127.35, 127.66, 128.22, 129.33, 129.52, 129.69, 132.18, 135.99, 136.49, 146.58, 149.44, 156.87. MS (EI) m/z (%): 374 (M⁺, 100), 373 (10), 224 (13), 121 (14), 77 (14). Anal. Calcd for C₂₀H₁₄N₄O₂S: C, 64.16; H, 3.74; N, 14.97; S, 8.57. Found: C, 64.33; H, 3.92; N, 15.26; S, 8.73. HRMS: m/z (EI) for C₂₀H₁₄N₄O₂S; calcd 374.0837; found: 374.0836.

3.2.5. 1-Naphthyl-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Cc. Dark red solid with metallic luster (91%). Mp: 156.7-157.3 °C. Recrystallization from acetone gave a dark red solid with metallic luster 159.0-161.0 °C. UV (EtOH): λ_{\max} nm (ϵ /M⁻¹ cm⁻¹) 498.0 (33,840), 282.0 (14,260). IR (Nujol) ν 1548, 1510, 1330, 1307, 1259, 1099, 850 cm⁻¹. ¹H NMR (DMSO-d₆) δ 6.90-6.94 (m, 1H, 4'-H), 7.12 (br d, 1H, J =8.4 Hz, Naphthyl-H), 7.19-7.39 (m, 6H, 3, 3', 5'-H, Naphthyl-H, 2''' and 6'''-H), 7.42-7.50 (m, 1H, Naphthyl-H), 7.52-7.58 (m, 1H, Naphthyl-H), 7.74 (t, 1H, J =8.1 Hz, Naphthyl-H), 7.83 (br d, 1H, J =8.1 Hz, Naphthyl-H), 8.08 (m, 3H, 4-H and 3''' and 5'''-H), 8.24 (br d, 1H, J =8.4 Hz, Naphthyl-H). ¹³C NMR (DMSO-d₆) δ 103.98, 112.80, 121.68, 121.79, 124.96, 125.69, 126.83, 127.17, 127.41, 127.92, 128.20, 128.28, 128.42, 130.36, 131.28, 131.76, 132.59, 133.64, 137.41, 146.49, 149.83, 156.65. MS (EI) m/z (%): 424 (M⁺, 100), 274 (29), 273 (17), 241 (14), 217 (7), 127 (11), 121 (22). Anal. Calcd for C₂₄H₁₆N₄O₂S: C, 67.91; H, 3.77; N, 13.20; S, 7.56. Found: C, 68.20; H, 3.92; N, 13.37; S, 7.80. HRMS: m/z (EI) for C₂₄H₁₆N₄O₂S; calcd 424.0994; found: 424.0986.

3.2.6. 1-(4''-Methoxyphenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Dc. Violet solid with gold luster (81%). Mp: 176.0-179.0 °C. Recrystallization from acetone gave a violet solid with gold luster 181.0-183.0 °C. UV (EtOH): λ_{\max} nm (ϵ /M⁻¹ cm⁻¹) 500.0 (37,580), 264.0 (9900), 228.0 (22,820). IR (Nujol) ν 3051, 2568, 1569, 1546, 1509, 1490, 1436, 1429, 1421, 1366, 1338, 1326, 1308, 1291, 1253, 1243,

1233, 1196, 1166, 1109, 1149, 1091, 1041, 1018, 982, 963, 850, 815, 771, 748, 734 cm^{-1} . ^1H NMR (Acetone- d_6) δ 3.95 (s, 3H, OCH_3), 6.97 (d, 1H, $J=4.5$ Hz, 3-H), 7.02-7.06 (m, 1H, 4'-H), 7.08 (d, 1H, $J=4.5$ Hz, 4-H), 7.13 (dd, 1H, $J=3.9$ and 1.2 Hz, 3'-H), 7.16 (d, 2H, $J=9.0$ Hz, 2'' and 6''-H or 3'' and 5''-H), 7.45 (d, 2H, $J=9.0$ Hz, 3'' and 5''-H or 2'' and 6''-H), 7.48 (dd, 1H, $J=5.1$ and 1.2 Hz, 5'-H), 7.71 (d, 2H, $J=9.2$ Hz, 2''' and 6'''-H), 8.29 (d, 2H, $J=9.2$ Hz, 3''' and 5'''-H). ^{13}C NMR (DMSO- d_6) δ 55.55, 103.51, 113.12, 114.53, 121.88, 125.16, 127.70, (2 overlapped signals), 128.32, 128.68, 130.73, 132.24, 137.31, 146.49, 149.66, 156.79, 159.96. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_4\text{O}_3\text{S}$: C, 62.38; H, 4.06; N, 13.60; S, 7.92. Found: C, 62.37; H, 3.96; N, 13.86; S, 7.93.

3.2.7. 1-(2'',4''-Dimethoxyphenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Ec. Dark violet solid with gold luster (84%). Mp: 185.0-187.0 $^\circ\text{C}$. Recrystallization from acetone gave a violet solid with gold luster 191.0-193.0 $^\circ\text{C}$. UV (EtOH): λ_{max} nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 507.0 (37,640), 279.0 (10,940), 223.0 sh(10,000). IR (Nujol) ν 1614, 1569, 1552, 1513, 1488, 1338, 1325, 1267, 1194, 1152, 1129, 1091, 1032, 1016, 977, 917, 855, 801, 747, 728, 686, 644, 621 cm^{-1} . ^1H NMR (Acetone- d_6) 3.72 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.75 (dd, 1H, $J=8.4$ and 2.4 Hz, 5''-H), 6.80 (d, 1H, $J=2.4$ Hz, 3''-H), 7.00 (d, 1H, $J=4.5$ Hz, 3-H), 7.03-7.07 (m, 1H, 4'-H), 7.08 (d, 1H, $J=4.5$ Hz, 4-H), 7.25 (dd, 1H, $J=3.9$ and 1.2 Hz, 3'-H), 7.36 (d, 1H, $J=8.4$ Hz, 6''-H), 7.45 (dd, 1H, $J=5.1$ and 1.2 Hz, 5'-H), 7.68 (d, 2H, $J=9.3$ Hz, 2''' and 6'''-H), 8.27 (d, 2H, $J=9.3$ Hz, 3''' and 5'''-H). ^{13}C NMR (CDCl_3) δ 55.98, 55.64, 99.64, 105.48 (two overlapped signals), 113.77, 116.84, 121.15, 127.68, 128.16, 129.49, 131.33, 131.98, 139.03, 128.16, 146.15, 148.82, 156.06, 156.90, 161.85. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_4\text{S}$: C, 60.82; H, 4.15; N, 12.90; S, 7.39. Found: C, 60.50; H, 4.27; N, 12.70; S, 7.38.

3.2.8 1-(3'',4'',5''-Trimethoxyphenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Fc. Green solid with metallic luster (88%). Mp: 208.4-209.3 $^\circ\text{C}$. Recrystallization from acetone gave a green solid with metallic luster 210.0-212.0 $^\circ\text{C}$. UV (EtOH): λ_{max} nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 499.0 (33520), 300.0 sh(5000). IR (Nujol) ν 1595, 1567, 1528, 1419, 1362, 1332, 1303, 1275, 1156, 1058, 1016, 985, 919, 873, 854, 805, 746, 716, 687, 633, 569, 524 cm^{-1} . ^1H NMR (Acetone- d_6) δ 3.89 (s, 6H, $2 \times \text{OCH}_3$), 3.96 (s, 3H, OCH_3), 7.11 (s, 2H, 2'' and 6''-H), 7.30-7.35 (m, 1H, 4'-H), 7.63 (d, 1H, $J=5.1$ Hz, 3-

H), 7.91 (d, 2H, $J=9.0$ Hz, 2''' and 6'''-H), 7.95 (br d, 1H, $J=3.3$ Hz, 3'-H), 7.98 (dd, 1H, $J=5.1$ and 1.2 Hz, 5'-H), 8.32 (d, 2H, $J=9.0$ Hz, 3''' and 5'''-H), 8.60 (d, 1H, $J=5.1$ Hz, 4-H). ^{13}C NMR (DMSO- d_6) δ 56.38, 60.49, 104.87, 107.55, 109.27, 114.01, 121.43, 125.17, 127.71, 128.63, 129.77, 130.98, 131.91, 138.56, 146.25, 149.17, 153.13, 156.03. MS (EI) m/z (%): 464 (M^+ , 100), 449 (28), 303 (13), 121 (26). Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$: C, 59.47; H, 4.30; N, 12.07; S, 6.91. Found: C, 59.65; H, 4.15; N, 11.85; S, 6.70. HRMS: m/z (EI) for $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_5\text{S}$; calcd 464.1154; found: 464.1154.

3.2.9. 1-(4''-Fluorophenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Gc.

Brown solid with metallic luster (90%). Mp: 184.0-185.0 °C. Recrystallization from acetone gave a brown solid with metallic luster 187.0-188.0 °C. UV (EtOH): λ_{max} nm ($\epsilon / M^{-1} \text{ cm}^{-1}$) 496.0 (33,580), 295.0 (9080), 261.0 (8580). IR (Nujol) ν 1615, 1553, 1513, 1434, 1354, 1327, 1287, 1234, 1193, 1106, 1042, 1023, 979, 852, 816, 803, 747, 708, 643, 629, 593, 570 cm^{-1} . ^1H NMR (Acetone- d_6) δ 7.00 (d, 1H, $J=4.2$ Hz, 3-H), 7.06-7.10 (m, 1H, 4'-H), 7.13 (d, 1H, $J=4.5$ Hz, 4-H), 7.14 (dd, 1H, $J=3.9$ and 1.2 Hz, 3'-H), 7.44 (t, 2H, $J=8.7$ Hz, 3'' and 5''-H), 7.53 (dd, 1H, $J=5.2$ and 1.2 Hz, 5'-H), 7.64 (dd, 2H, $J=9.1$ and 4.8 Hz, 2'' and 6''-H), 7.74 (d, 2H, $J=9.0$ Hz, 2''' and 6'''-H), 8.32 (d, 2H, $J=9.0$ Hz, 3''' and 5'''-H). ^{13}C NMR (DMSO- d_6) δ 104.51, 113.83, 116.37 and 116.22 (d, $J=23$ Hz, C3'', C5''), 121.68, 125.12, 127.83, 128.32, 129.19, 131.74 and 131.86 (d, $J=9.2$ Hz, C2'', C6''), 131.13, and 132.09 (d, $J=3.2$ Hz, C1''), 137.79, 146.47, 149.28, 156.24, 160.86 and 164.13 (d, $J=245$ Hz, C4''). MS (EI) m/z (%): 392 (M^+ , 100), 242 (3), 231 (6), 204 (5), 121 (78), 95 (5). Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{FN}_4\text{O}_2\text{S}$: C, 61.21; H, 3.32; N, 14.28; S, 8.18. Found: C, 61.13; H, 3.15; N, 14.50; S, 8.37. HRMS: m/z (EI) for $\text{C}_{20}\text{H}_{13}\text{FN}_4\text{O}_2\text{S}$; calcd 392.0743; found: 392.0734.

3.2.10. 1-(4''-Bromophenyl)-2-(2'-thienyl)-5-(4'''-nitrophenylazo)pyrrole 3Hc.

Dark brown solid with metallic luster (74%). Mp: 192.2-196.6 °C. Recrystallization from acetone gave a brown solid with metallic luster 198.0-199.0 °C. UV (EtOH): λ_{max} nm ($\epsilon / M^{-1} \text{ cm}^{-1}$) 492.0 (22,080), 292.0 (8980), sh 227.0 (19,100). IR (Nujol) ν 1512, 1488, 1462, 1428, 1380, 1241, 1228, 1195, 1149, 1102, 1068, 1040, 1023, 1006, 977, 844, 824, 803, 791, 747, 705, 690, 596, 506 cm^{-1} . ^1H NMR (Acetone- d_6) δ 7.14-7.17 (m, 1H, 4'-H), 7.20 (d, 1H, $J=4.8$ Hz, 3-H), 7.38 (br d, 1H, 3'-H), 7.61 (2

overlapped doublets, 3H, $J = 8.7$ Hz, 2'', 6''-H and 4-H), 7.69 (dd, 1H, $J = 4.8$ and 1.2 Hz, 5'-H), 7.80 (d, 2H, $J = 9.3$ Hz, 3'' and 5''-H), 7.89 (d, 2H, $J = 8.7$ Hz, 2''' and 6'''-H), 8.32 (d, 2H, $J = 9.3$ Hz, 3''' and 5'''-H). ^{13}C NMR (DMSO- d_6) δ 103.48, 113.38, 121.99, 122.83, 125.09, 127.73, 127.75, 128.54, 131.66, 131.85, 132.31, 135.29, 136.47, 146.65, 149.23, 156.69. MS (IE) m/z (%): 453 ($M^{+81}\text{Br}$, 79), 451 ($M^{+79}\text{Br}$, 80), 380 (4), 304 (5), 237 (7), 223 (7), 157 (6), 121 (100), 76 (5). Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{BrN}_4\text{O}_2\text{S}$: C, 52.98; H, 2.87; N, 12.36; S, 7.08. Found: C, 53.20; H, 2.75; N, 12.50; S, 7.33. HRMS: m/z (EI) for $\text{C}_{20}\text{H}_{13}^{79}\text{BrN}_4\text{O}_2\text{S}$; calcd 451.9943; found 451.9942.

3.3. Diazo coupling of thienylpyrrole 1D with 2,4-dinitro-substituted aryldiazonium salt 2d

i) Diazotisation of 2,4-dinitroaniline

NaNO_2 (4.0 mmol) was added gradually to concentrated sulfuric acid (5 ml) and the mixture was heated to 70 °C. The resultant solution was allowed to cool to 35 °C before 2,4-dinitroaniline (4.0 mmol) was added, then stirred to room temperature for 1.5 h, and poured onto crushed ice (7 g). The aqueous solution (containing 4.0 mmol of diazonium salt) was filtered before use in coupling experiments.

ii) Coupling with thienylpyrrole 1D

The diazonium salt solution previously prepared (4.0 mmol) was added drop wise to the solution of thienylpyrrole 1D (4.0 mmol) in acetonitrile (50 ml) and acetic acid (15 ml) and the combined solution maintained at 0 °C for 3h with stirring. After this time the resulting mixture was diluted with petrol ether (20 ml) and water (40 ml) and the product formed was isolated by filtration. The organic layer was diluted with chloroform, washed with water and dried with anhydrous MgSO_4 . The dried solution was evaporated and the remaining 1-aryl-2-(2'-thienyl)-5-(2''',4'''-dinitrophenylazo)pyrrole 3Dd was purified by column chromatography on silica with increasing amounts of ether in light petroleum as eluent.

3.3.1. 1-(4''-Methoxyphenyl)-2-(2'-thienyl)-5-(2''',4'''-dinitrophenylazo)pyrrole 3Dd. Dark violet solid (47%). Mp: 145.0-146.0 °C. Recrystallization from acetone gave

a dark violet with metallic luster 148.0-149.0 °C. UV (EtOH): λ_{max} nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) 531.0 (38,420), 298.0 (7480), 226.0 (24,860). IR (Nujol) ν 1593, 1515, 1455, 1417, 1378, 1345, 1322, 1257, 1187, 1167, 1133, 1017, 998, 919, 895, 842, 809, 776, 741, 708 cm^{-1} . ^1H NMR (Acetone- d_6) δ 3.99 (s, 3H, OCH₃), 7.10-7.14 (m, 1H, 4'-H), 7.13 (d, 1H, $J=4.8$ Hz, 3-H), 7.17 (d, 1H, $J=4.8$ Hz, 4-H), 7.20 (d, 2H, $J=9.0$ Hz, 3'' and 5''-H, or 2'' and 6''-H), 7.33 (dd, 1H, $J=3.6$ and 1.2 Hz, 3'-H), 7.50 (d, 2H, $J=9.0$ Hz, 3'' and 5''-H, or 2'' and 6''-H), 7.59 (dd, 1H, $J=5.1$ and 1.2 Hz, 5'-H), 7.63 (d, 2H, $J=9.0$ Hz, 6'''-H), 8.44 (dd, 1H, $J=9.3$ and 2.7 Hz, 5'''-H), 8.71 (d, 1H, $J=2.7$ Hz, 3'''-H). ^{13}C NMR (CDCl₃) δ 55.97, 114.48, 115.36, 119.45, 119.69, 120.49, 127.86, 128.49, 128.99, 129.33, 129.63, 129.94, 131.41, 132.26, 133.19, 140.61, 146.46, 150.19, 161.61. MS (EI) m/z (%): 449 (M⁺ 100), 403 (42), 281 (17), 254 (25), 121 (56). Anal. Calcd for C₂₁H₁₅N₅O₅S: C, 56.10; H, 3.34; N, 15.59; S, 7.14. Found: C, 56.23; H, 3.14; N, 15.80; S, 7.32. HRMS: m/z (EI) for C₂₁H₁₅N₅O₅S; calcd 449.0794; found 449.0783.

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Captions

Table 1. Yields and UV-vis absorption spectra of 1-alkyl(aryl)-2-(2'-thienyl)-5-(phenylazo)pyrroles **3** and thienylpyrroles **1**.

*All the UV-vis spectra were recorded in ethanol.

Table 2. Solvatochromic data [λ_{\max} (nm) and ν_{\max} (cm^{-1}) of the charge-transfer band] for **3Dc**, in 15 solvents in comparison with π^* values by Kamlet and Taft.³⁶

^a The correlation coefficient r obtained for the linear solvation energy relationship with π^* values by Kamlet and Taft for aliphatic and dipolar aprotic solvents was $r = 0.9750$. This value was obtained without the alcohols, aromatic and chlorinated solvents^{9,38} which deviate slightly from the regression line.

Table 3. Electrochemical data for thienylpyrroles **1** and thienylpyrrole azo dyes **3**.

^a Measurements were carried out in *N,N*-dimethylformamide containing 0.1 mol dm^{-3} $[\text{NBu}_4][\text{BF}_4]$ as base electrolyte at a carbon working electrode with a scan rate of 0.1 V s^{-1} . Ferrocene was added as an internal standard at the end of each measurement, and all E values are quoted in volts *versus* the ferrocinium/ferrocene-couple.

Figure 1. Cyclic voltammograms of **3Da** and **3Dc**, recorded in *N,N*-dimethylformamide containing 0.1 mol dm^{-3} $[\text{NBu}_4][\text{BF}_4]$ at a vitreous carbon electrode (area = 0.049 cm^2). Scan rate = 0.1 V s^{-1} .

Entry	R ₁	R ₂	Compound	λ_{max}^* [nm] (ϵ)	Compound	Yield (%)	λ_{max}^* [nm] (ϵ)
1	4-methoxyphenyl	4-CO ₂ Me	---	---	3Da	85	473.0 (31700)
2	4-methoxyphenyl	4-CN	---	---	3Db	84	479.0 (37640)
3	<i>n</i> -propyl	4-NO ₂	1A	291.0 (1800)	3Ac	63	488.0 (25100)
4	phenyl	4-NO ₂	1B	294.5 (9208)	3Bc	70	497.0 (33480)
5	naphthyl	4-NO ₂	1C	288.5 (15638)	3Cc	34	498.0 (33840)
6	4-methoxyphenyl	4-NO ₂	1D	290.0 (11410)	3Dc	81	500.0 (37580)
7	2,4-dimethoxyphenyl	4-NO ₂	1E	286.5 (10093)	3Ec	84	507.0 (33640)
8	3,4,5-trimethoxyphenyl	4-NO ₂	1F	281.5 (8477)	3Fc	88	499.0 (33520)
9	4-fluoro	4-NO ₂	1G	293.0 (8505)	3Gc	90	496.0 (33580)
10	4-bromo	4-NO ₂	1H	289.5 (7939)	3Hc	31	492.0 (22080)
11	4-methoxyphenyl	2,4-diNO ₂	---	---	3Dd	47	531.0 (38420)

Table 1

Table 2

Solvents	π^*a	Compound	
		λ_{\max}	ν_{\max}
<i>n</i> -Hexane	-0.008	478.0	20,920
Cyclohexane	0.00	485.0	20,618
Diethyl ether	0.27	490.0	20,408
Dioxane	0.55	496.0	20,161
Ethyl acetate	0.55	496.0	20,161
Tetrahydrofuran	0.58	500.0	20,000
Acetone	0.71	500.0	20,000
Acetonitrile	0.75	508.0	19,685
Dimethylformamide	0.88	510.0	19,607
Dimethylsulfoxide	1.00	516.0	19,379
Ethanol	0.54	500.0	20,000
Methanol	0.60	500.0	20,000
Chloroform	0.58/0.76 ³⁷	531.0	18,832
Dichloromethane	0.82	528.0	18,939
Toluene	0.54	497.0	20,120

Table 3

Thienylpyrroles 1		Thienylpyrrole azo dyes 3				
Oxidation ^a		Reduction ^a			Oxidation ^a	
Compound	E _{pa} / V	Compound	- ¹ E _{1/2} / V	- ² E _{1/2} / V	¹ E _{pa} / V	² E _{pa} / V
—	—	3Da	1.71	—	0.57	0.87
—	—	3Db	1.74	—	0.59	0.88
1A	0.57	3Ac	1.23	1.70	0.78	0.96
1B	0.53	3Bc	1.29	1.76	0.72	0.93
1C	0.54	3Cc	1.31	1.80	0.72	0.92
1D	0.48	3Dc	1.35	1.83	0.62	0.90
1E	0.45	3Ec	1.36	1.77	0.61	0.90
1F	0.46	3Fc	1.35	1.81	0.63	0.91
1G	0.55	3Gc	1.27	1.73	0.80	0.96
1H	0.54	3Hc	1.25	1.72	0.79	0.97
—	—	3Dd	1.40	1.76	0.68	0.93

Schemes

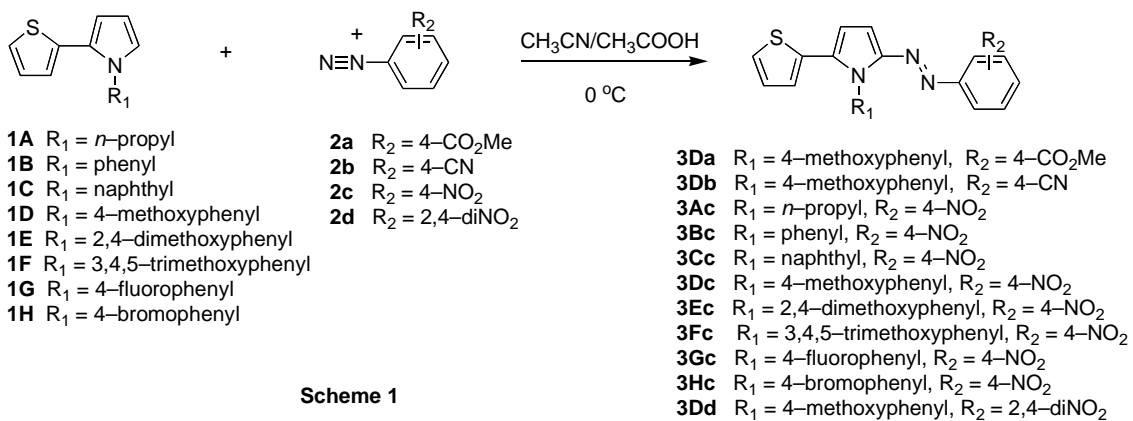


Figure 1

