

New pyrimidines incorporating thiophene and pyrrole moieties: synthesis and electrochemical polymerization

Anastasiya Yu. Bushueva,^a Elena V. Shklyueva^b and Georgii G. Abashev^{*a,b}

^a Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, 614013 Perm, Russian Federation. Fax: +7 342 237 8262; e-mail: gabashev@psu.ru

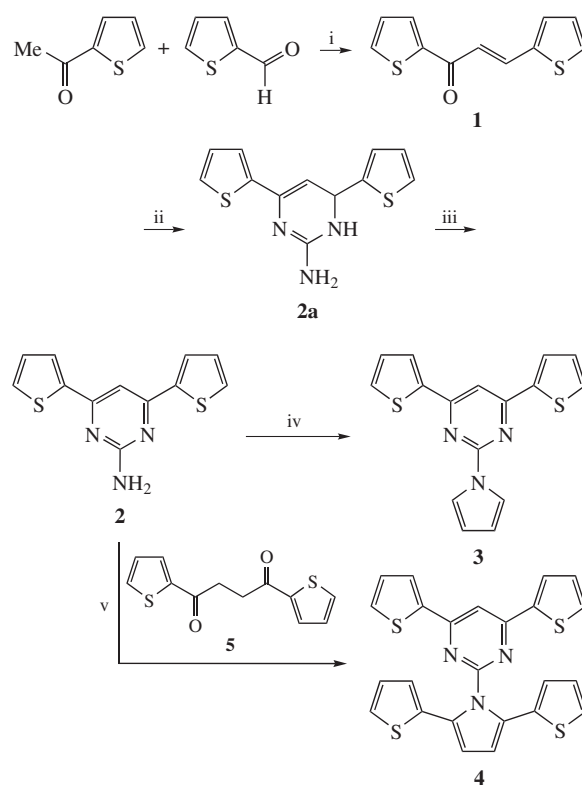
^b Institute of Natural Sciences, Perm State University, 614990 Perm, Russian Federation. Fax: +7 342 239 6481

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The synthesis and electrochemical polymerization on the indium–tin oxide covered glass plates of two new substituted pyrimidines, namely, (1*H*-pyrrol-1-yl)-4,6-di(thiophen-2-yl)pyrimidine and [2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl]-4,6-di(thiophen-2-yl)pyrimidine was performed; the structure of the latter was determined by X-ray methods.

Since the discovery of electroconductivity in poly(acetylene), the organic conducting polymers attract the attention of researchers. Conducting polymers find application in the construction of organic light emitting diodes,¹ nonlinear optic materials,^{2,3} organic field-effect transistors,³ photovoltaic cells,^{4,5} electrochromic devices and various types of sensors. Of all the conducting polymers, poly(thiophenes) have come into close attention because of their chemical stability, simplicity in performing synthetic procedures and subsequent structure modifications. Among the scope of the electroconducting polymers, the ones incorporating various aromatic carbo- and heterocyclic fragments are of considerable importance as different combinations of these fragments allows one to modify the electrophysical, optical and other properties of a future polymer.¹ The introducing of heteroaryl moieties into the extended π -systems results in generation of new interesting properties important for optoelectronics. High electron affinity of some heterocycles is widely applied in the design of materials with electronic (*n*) type of conductivity. Various substituted pyridines, triazines, 1,3,4-oxadiazoles, quinolines and quinoxalines are in extensive use for this purpose, but pyrimidine units are found to be rarely incorporated into conjugated molecular ensembles.⁶ One of the first works concerning the application of pyrimidines for blue light-emitting devices was fulfilled by K. T. Wong *et al.*:⁷ conjugated oligomers with an alternating phenylene-pyrimidine structure have been synthesized by the successive Suzuki coupling reaction starting from 2-bromo-5-iodopyrimidine and applied for fabrication of blue light-emitting electroluminescent devices. New pyrimidine-containing oligo(arylene)s, notably the pyrimidine–fluorene hybrid systems have been synthesized and described;⁶ an organic light-emitting diode with one of these new compounds applied as an emissive layer has been fabricated in the configuration indium–tin oxide (ITO)/poly(ethylenedioxythiophene)/polymer/Ca/Al. Interesting fluorescent properties, as well as solvatofluorochromism, have been manifested by a set of the newly prepared 2,4,6-triarylpyrimidines.⁸ Banana-shaped and star-shaped bis- or tris(arylethynyl)pyrimidine oligomers and their light-emitting properties were reported.⁹

The monomers, which include electron-deficient heterocycles such as pyrimidines and pyridines, as well as oxadiazoles sandwiched between electron-rich units (*e.g.*, thiophenes and pyrroles) provide the opportunity to tune the properties of a further polymer: incorporation of external π -rich unites into monomer affords polymers that can be both *p*- and *n*-doped.¹⁰ Such polymers are of great interest because emitting devices constructed



Scheme 1 Reagents and conditions: i, 2% aqueous NaOH, reflux, 2 h; ii, [(NH₂)₂C=NH]₂H₂SO₄, 50% aqueous KOH, EtOH, reflux, 1 h; iii, H₂O₂, reflux, 1 h, cold water; iv, 2,5-dimethoxytetrahydrofuran, AcOH, reflux, 1 h; v, toluene, *p*-toluenesulfonic acid, reflux, 24 h, TLC control; vi, thiophene, AlCl₃, CH₂Cl₂ (dry), 15–20 °C, 4 h stirring at room temperature.

from them require fewer layers than usual ones and this fact can result in increasing the device efficiency. Here, we present the synthesis and electrochemical investigation of new monomers consisting of π -deficient pyrimidine core surrounded with π -rich heteroaryl moieties – pyrrole and thiophene.

The chemical transformations leading to compounds **3** and **4** are summarized in Scheme 1.

The mixture of chalcone **1** and guanidine sulfate in ethanol was heated under reflux for 1 h in the presence of 50% aqueous KOH to give intermediate compound **2a**, which was oxidized *in situ* with formation of 2-amino-4,6-di(thiophen-2-yl)pyrimidine **2**.¹¹ After cooling, the precipitated compound **2** was

filtered off and chromatographically purified.[†] The primary amino group of pyrimidine **2** was used first for the construction

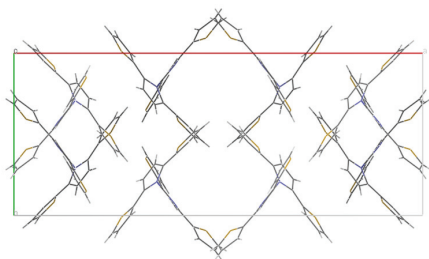


Figure 1 Crystal packing of compound **4** (view along the *c* axis).

[†] The ¹H NMR and UV spectra were recorded on a Mercury plus300 spectrometer (GMDS as internal standard) and a SF-2000 UV-VIS spectrophotometer (OKB Spectr), respectively. Mass spectra were recorded on an Agilent GC 6890N MSD 5975B instrument (EI, 70 eV).

2-(1*H*-Pyrrol-1-yl)-4,6-di(thiophen-2-yl)pyrimidine 3. The 2 h refluxing of 2-acetylthiophene (3.79 g, 0.03 mol, 3.3 ml) and thiophene-2-carboxyaldehyde (3.36 g, 0.03 mol, 2.83 ml) in 2% aqueous NaOH (450 ml) gave rise to 1,3-di(thiophen-2-yl)propenone **1**, which was filtered off on cooling of the reaction mixture, thoroughly washed with water, air dried and used further without purification. Chalcone **1** (5.5 g, 0.025 mol), guanidine sulfate (4.1 g, 0.019 mol), ethanol (60 ml) and 50% aqueous KOH solution (20 ml) were mixed together and then heated up at a reflux temperature for 1 h. Under the same conditions 30–33% aqueous H₂O₂ (9 ml) was slowly added to the above mixture over a period of 1 h. Still the hot reaction mixture was poured into ice water. The resulting precipitate of 2-amino-4,6-di(thiophen-2-yl)pyrimidine **2** was filtered off, thoroughly washed with cold water and purified by column chromatography (silica gel, CH₂Cl₂) to give **2** as pale yellow crystals. Yield 59%, mp 173–174 °C. ¹H NMR (CDCl₃) δ: 5.08 (br. s, 2H, NH₂), 7.13 (t, 2H, thiophene, *J* 3.9 Hz), 7.24 (s, 1H, CH, pyrimidine), 7.45, 7.47 (dd, 2H, thiophene, *J* 5.4 Hz), 8.74 (dd, 2H, thiophene, *J* 3.9 Hz). ¹³C NMR (CDCl₃) δ: 100.71, 126.90, 128.02, 129.08, 142.95, 160.47. MS, *m/z*: 260.05 (18.5), 295 (100) [M⁺] (C₁₂H₉N₃S₂), 258 (39), 218.05 (39.6), 108.05 (11.1). Pyrimidine **2** (1.30 g, 0.005 mol) was dissolved in the minimum amount of glacial acetic acid, then mixed with 2,5-dimethoxytetrahydrofuran (0.66 g, 0.005 mol, 0.65 ml) and refluxed for 1 h. Thus obtained reaction mixture was thereafter poured into ice water and extracted with CH₂Cl₂ (3×75 ml). The combined organic layers were washed with water and aqueous NaHCO₃ and dried with Na₂SO₄. The solvent was then evaporated off and a residue was chromatographically purified (silica gel; CH₂Cl₂–hexane, 1:1) to give target product **3** as pale yellow crystals. Yield 55%, mp 143–145 °C. ¹H NMR (CDCl₃) δ: 6.35 (t, 2H, pyrrole, *J* 2.4 Hz), 7.17 (t, 2H, thiophene, *J* 3.9 Hz), 7.52, 7.54 (dd, 2H, thiophene, *J* 5.4 Hz), 7.53 (s, 1H, pyrimidine), 7.84, 7.85 (dd, 2H, thiophene), 7.89 (t, 2H, pyrrole, *J* 2.4 Hz). ¹³C NMR (CDCl₃) δ: 104.55, 111.54, 119.12, 127.48, 128.192, 130.07, 142.1, 160.22. MS, *m/z*: 311 (10.7), 310 (20.3), 309 (100) [M⁺] (C₁₆H₁₁N₃S₂), 135 (16.1).

2-[2,5-Di(thiophen-2-yl)-1*H*-pyrrol-1-yl]-4,6-di(thiophen-2-yl)pyrimidine 4. Suspension of compounds **5** (1.15 g, 0.0046 mol), **2** (1.66 g, 0.0064 mol) and *p*-toluenesulfonic acid (0.10 g, 0.00053 mol) in dry toluene (20 ml) was refluxed for about 24 h under TLC control. The following evaporation of toluene gave rise to the crude target product **4** as a residue which was chromatographically purified (silica gel; CH₂Cl₂–hexane, 1:1) to give compound **4** as bright yellow crystals. Yield 25%, mp 175–177 °C. ¹H NMR (CDCl₃) δ: 6.49 (s, 2H, pyrrole), 6.83 (t, 2H, thiophene, *J* 3.6 Hz), 6.90 (t, 2H, thiophene, *J* 2.7 Hz), 7.07–7.12 (m, 4H, thiophene), 7.48 (d, 2H, thiophene, *J* 3.9 Hz), 7.60 (s, 1H, pyrimidine), 7.71 (d, 2H, thiophene, *J* 3.6 Hz). Used in this synthetic procedure 1,4-di(thiophen-2-yl)-1,4-butane-1,4-dione **5** was prepared as follows: solution of thiophene (48 ml, 0.6 mol) and succinyl dichloride (28 ml, 0.25 mol) in CH₂Cl₂ (100 ml) was added dropwise to a stirred AlCl₃ (80 g, 0.6 mol) suspension in the same solvent (250 ml) with the rate enabling to keep the reaction mixture temperature at a level of 15–20 °C. The stirring was then continued for 4 h. After that the reaction mixture was poured into ice (1 kg), containing conc. HCl (25–30 ml), additionally stirred for ~0.5 h and extracted with CH₂Cl₂. The combined organic layers were washed with water and aqueous NaHCO₃, dried with MgSO₄, saturated in a vacuum and the residue was recrystallized from ethanol to give compound **5** as bluish crystals. Yield 70%, mp 131–133 °C (lit.,¹⁵ 130–133 °C).

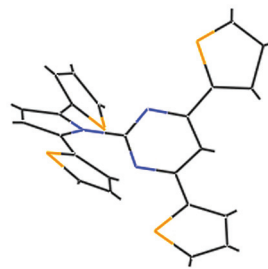


Figure 2 Molecular structure of compound **4**.

of *N*-substituted pyrrole ring. One-hour refluxing of compound **2** with dimethoxytetrahydrofuran in a minimal amount of glacial acetic acid resulted in generation of monomer **3**, while the interaction of this compound with 1,4-di(thiophen-2-yl)butane-1,4-dione **5**^{12,13} in toluene (*p*-toluenesulfonic acid as a catalyst) allowed us to obtain interesting monomer **4**, in which a pyrimidine core is surrounded by five π -rich heterocycles (four thiophene and one pyrrole moieties). All prepared compounds are air-stable solids easily soluble in common organic solvents such as THF, CHCl₃, CH₂Cl₂, MeCN and Me₂CO and were characterized by NMR spectroscopy. The molecular structure of compound **4** was proved by X-ray analysis. Crystal packing of **4** is shown in Figure 1. The molecule of this compound is non-planar and has the shape of a curved propeller (Figure 2).[‡]

Pyrimidine **4** was examined by chromatography–mass spectrometry. It has been shown that this compound is not heat-resistant: its complete thermal degradation with formation of fragments of different mass values was observed at 350 °C. Mass spectrum, *m/z*: 427, 365, 352, 259, 242, 218, 134.

The electrochemical behaviour of compounds **2–4** was studied by cyclic voltammetry in acetonitrile solution at room temperature using Et₄N⁺ClO₄[−] (0.1 mol dm^{−3}) as a supporting electrolyte.[§] All measurements were conducted in the electrochemical cell with an ITO (or glassy carbon) electrode as the working electrode, a platinum wire – as the counter electrode and Ag/AgCl

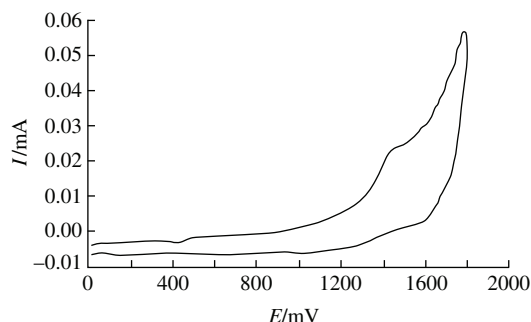


Figure 3 Cyclic voltammogram of compound **2** ($V_{\text{scan}} = 100 \text{ mV s}^{-1}$, [Et₄NClO₄] = 0.1 mol dm^{−3}, [**2**] = $1 \times 10^{-5} \text{ mol dm}^{-3}$).

[‡] Crystal data for **4**. Crystals of **4** (orange plates) (C₂₄H₁₅N₃S₄, *M_r* = 473.66) are monoclinic, space group *C2/c*, *a* = 29.969(3), *b* = 11.7252(15) and *c* = 12.4358(14) Å, β = 100.685(9)°, *V* = 4294.0 Å³, *Z* = 8. The X-ray diffraction data were collected at 295(2) K on a Xcalibur-3 (Oxford Diffraction) automated diffractometer using graphite monochromated MoK α (λ = 0.71073 Å) radiation. *R*-factor (%) 4.31, total reflection number 4340. The structure was solved by direct method using the SHELXS-97 program and refined by the full matrix least-squares using the SHELXL-97 program.¹⁶ Figures were made using the Mercury 1.4.2 program.

CCDC 752297 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

[§] Potentiostat-galvanostat 'IPC-compact' with voltammetric stand EM-04 was used for electrochemical measurements. Obtained data were processed by the IPC-compact 8.60F program.

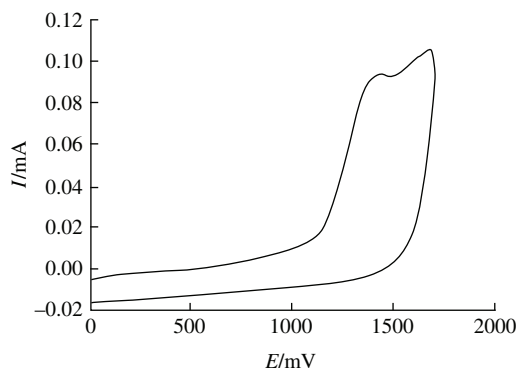


Figure 4 Cyclic voltammogram of compound **3** ($V_{\text{scan}} = 100 \text{ mV s}^{-1}$, $[\text{Et}_4\text{NClO}_4] = 0.1 \text{ mol dm}^{-3}$, $[\mathbf{3}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$).

electrode – as the reference one. The scan rate (V_{scan}) was 100 mV s^{-1} . For ITO electrodes, we used glassy plates coated on one surface by indium–tin oxide layer with $R_s = 8\text{--}12 \Omega$ from Aldrich. Rectangular shapes were cut out from plates and used as the working electrode after the cleaning procedure (washing with water, acetone, dichloromethane for about 15 min each). All the prepared thiophene–pyrimidine or thiophene–pyrimidine–pyrrole heterocycles supposedly undergo one-electron oxidation with cation-radical formation (Figures 3–5). Such a mechanism is thought to be the most credible reasoning from the behaviour of compounds of similar structure.¹⁴ The E_{pa} values for compounds **2** and **3** are rather high and practically equal (about 1435 mV) (Figures 3 and 4). The pyrimidine **3**, including a pyrrole moiety, forms a stable blue film.

Incorporation of an electron-rich 2,5-di(thiophen-2-yl)pyrrol-1-yl fragment into a pyrimidine core (compound **4**) results in a sharp decrease in E_{pa} for this heterocycle (908 mV). As a consequence, this compound is readily polymerized to give a stable green polymer film on the ITO surface (Figure 5). This film was investigated by UV-VIS spectroscopy: the polymeric character

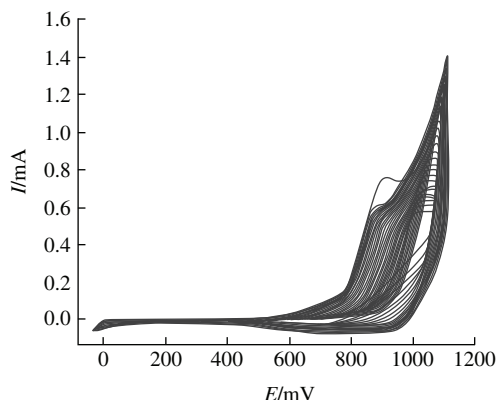


Figure 5 Electropolymerization of compound **4** ($V_{\text{scan}} = 100 \text{ mV s}^{-1}$, $[\text{Et}_4\text{NClO}_4] = 0.1 \text{ mol dm}^{-3}$, $[\mathbf{4}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$).

of a film formed on the ITO surface was confirmed by existence of a bathochromic shift in its absorption spectrum. The following absorption maxima for poly(**4**) were found: $\lambda_{\text{max}}^1 = 309.9 \text{ nm}$ and $\lambda_{\text{max}}^2 = 345.9 \text{ nm}$, while for monomer **4** these values were 228.1 and 338.5 nm, respectively.

Thus, we have synthesized two new substituted pyrimidines including different combination of electron-donating heterocyclic moieties. [2,5-Di(thiophen-2-yl)-1*H*-pyrrol-1-yl]-4,6-di(thiophen-2-yl)pyrimidine can easily undergo electropolymerization to give a stable electroconducting film. A propeller-shaped crystal structure of this compound has been determined by X-ray analysis.

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