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Thiophene-containing monomers for the synthesis of new polythiopheneferrocenes*,**

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Synthesis of arylenebis(2-aminothiophene-3-carbonitriles) by the Gewald reaction was developed. The structures of the synthesized monomers were established by IR and NMR spectroscopy, mass spectrometry, and microanalysis. Polycondensation of these monomers with diacetylferrocene gave azomethine-bridged polythiopheneferrocenes.

Key words: arylenebis(2-aminothiophene-3-carbonitriles), ferrocene, Gewald reaction, polycondensation.

Metal complex compounds, *viz*., ferrocene, are widely used as different functional materials: conducting and magnetic molecular materials,[1—3] dyes and pigments,[4,5] nonlinear optical materials,[6—9] electroactive substrates,[10] *etc*. One of the approaches to increase the electron delocalization is introduction of the thiophene residues into the ferrocene environment. It should be noted that employment of different building blocks and bridging groups during synthesis of the coordination polymers allow prediction and control of the formation of the corresponding supramolecular assemblies and frameworks.[11—13]

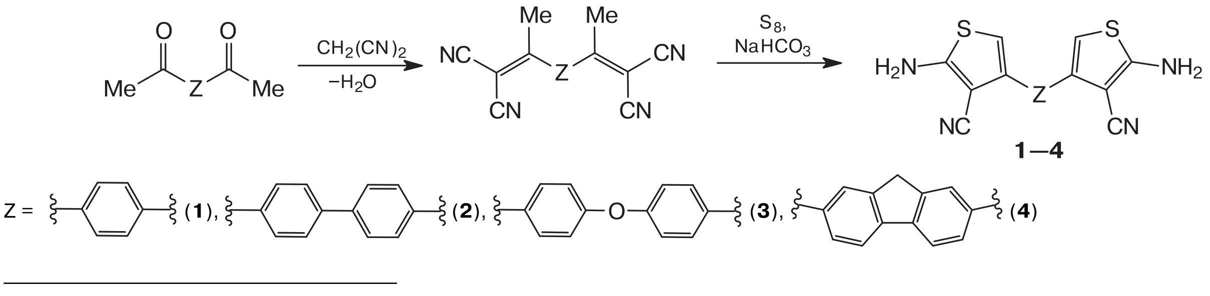
The aim of the present work is to develop the synthesis of thiophene-containing bis-*ortho*-amino nitriles *via* the Gewald reaction and to use these monomers in the subsequent polycondensation with 1,1′-diacetylferrocene, which can give access to new azomethine-bridged polythiopheneferrocenes.

Results and Discussion

2-Aminothiophene and its substituted analogs can be prepared by the reduction of 2-nitrothiophene, azide cleavage, oxime rearrangement, and aminolysis of 2-halo- and 2-mercaptothiophenes, and by ring closure of various sulfur-containing derivatives.[13] In the present work, we synthesized 2,2′-diamino(bisthiophenes) by the Gewald reaction[14,15] between such methylcarbonyl compounds as bisacetophenones and malononitrile in the presence of elemental sulfur and $NaHCO_3$ as the base (Scheme 1).

Diamino dinitriles **1—4** are beige or light brown powders that have sharp melting points. They are soluble in benzene, amide solvents, and DMSO and insoluble in hexane, EtOH, and water. The structures of compounds **1—4** were confirmed by microanalysis, IR and NMR spectroscopy, and mass spectrometry. The IR spectra of compounds **1—4** show the absorption bands of the valence and deformation

Scheme 1



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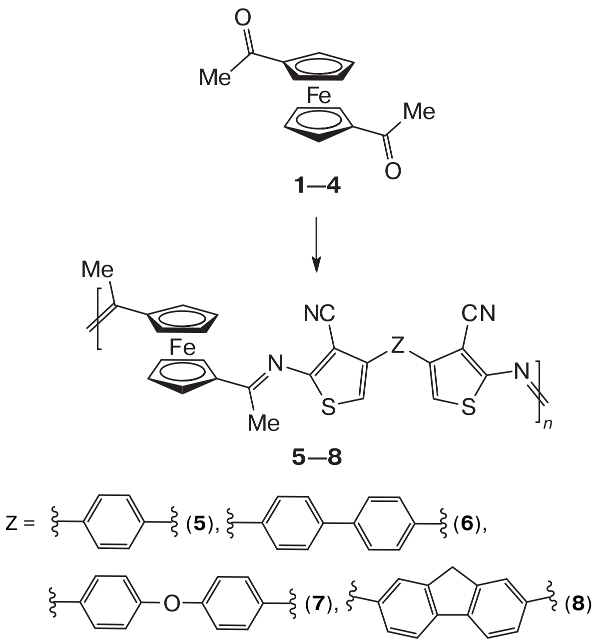
vibrations of the N—H bond at *ca*. 3330 and 1280 cm^{-1}, respectively, and the intense absorption bands of the valence vibrations of the conjugated CN group at *ca*. 2230 cm^{-1}. The ^1H NMR spectra of compounds **1—4** exhibit the singlet signal of the H(5) thiophene ring proton at the δ 6.51—6.62 range and the broadened singlets of the NH_2 group at the δ 7.12—7.32 range. Molecular masses of the synthesized compounds determined by mass spectrometry based on the *m/z* ratios of the molecular ions correspond to the calculated values.

It is of note that nitrile-containing monomers are emitted in the red spectral range that may be promising for their use as optically active materials.[16]

Azomethine-bridged polythiopheneferrocenes **5—8** were synthesized by polycondensation of diamino dinitrile thiophenes **1—4** with diacetylferrocene in toluene (Scheme 2).

Scheme 2



Polymers **5—8** are yellow-brown powders with logarithmic viscosity of 0.11—0.18 dL g^{-1}, which are soluble in the amide solvents. The IR spectra of compounds **5—8** contain the absorption bands of the valence and deformation vibrations of the amino groups at *ca*. 700 and 3340 cm^{-1} and the bands of the azomethine bond C—N vibrations at *ca*. 1390 cm^{-1}. The intense absorptions at *ca*. 1730 cm^{-1} were attributed to the carbonyl group vibrations and the absorptions at the 2220—2240 cm^{-1} range were assigned to the CN group vibrations.

Thermogravimetric analysis performed in air indicated that polyazomethines **5—8** lost 5% of their weight at 300—350 °C. Above 600 °C, the polymers decomposed to give black char residues in the amount of 15—20% with respect to the initial sample weights. It is known that heating of ferrocene-containing polymers at 300—400 °C for 5—6 h in air gives magnetite.[17] Therefore, we plan to study the magnetic properties of polymers **5—8**.

In summary, in the present work we synthesized arylenebis(2-aminothiophene-3-carbonitriles). These monomers were used to prepare new azomethine-bridged polythiopheneferrocenes, which are promising precursors of the magnetic materials.

Experimental

1,1′-Diacetylferrocene, 1,4-diacetylbenzene, 4,4′-diacetylbiphenyl, 4,4′-diacetyldiphenyl oxide, and 1,9-diacetylfluorene were purchased from Sigma-Aldrich. Malononitrile (Aldrich) and elemental sulfur were used as purchased.

The starting bis-ylidenemalononitrile derivatives were synthesized by the Knoevenagel reaction of diacetyl compounds with malononitrile as earlier described.[18]

^1H NMR spectra were recorded with a Bruker AMX-400 instrument in DMSO-d_6, the chemical shifts are given in the δ scale relative to Me_4Si. IR spectra were recorded with a Bruker Vertex 70v FTIR spectrometer. Mass spectrometry was performed with a RRATOS MS-890 instrument. Thermogravimetric analysis was performed on a Netzsch DSC Jupiter STA 449 F3 thermal analyzer.

Synthesis of thiophene-containing bis-*ortho*-amino nitriles 1—4 (general procedure). A mixture of the corresponding bis-ylidenemalononitrile (0.01 mol) and elemental sulfur (0.012 mol) was suspended in THF (10 mL). The resulting suspension was heated to 35 °C and 10% aqueous $NaHCO_3$ (10 mL) was slowly added over 1 h. After all the $NaHCO_3$ solution was added, the mixture was stirred at 40 °C for 1 h and then kept for 24 h. The obtained residue was collected by filtration and washed with water until neutral. Products **1—4** were recrystallized from DMF and then purified by liquid—solid extraction with acetone using a Soxhlet apparatus.

4,4′-(1,4-Phenylene)bis(2-aminothiophene-3-carbonitrile) (1) was synthesized from 1,4-diacetylbenzene bis-ylidenemalononitrile (2.58 g, 0.01 mol). Yield 2.40 g (76%), m.p. 263—265 °C. Found (%): C, 59.72; H, 3.29; N, 17.21; S, 20.11. $C_{16}H_{10}N_4S_2$. Calculated (%): C, 59.61; H, 3.13; N, 17.38; S, 19.89. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 323 $[M + H]^+$ (100). IR, ν/cm^{-1}: 3320 (N—H_{val}), 2220 (CN), 1530 (Ar), 1280 (N—H_{def}). ^1H NMR, δ: 6.62 (s, 2 H, thiophene), 7.20 (br.s, 4 H, NH_2), 7.62 (d, 4 H, C_6H_4, J = 2.0 Hz).

4,4′-[(1,1′-Biphenyl)-4,4′-diyl]bis(2-aminothiophene-3-carbonitrile) (2) was synthesized from 4,4′-diacetylbiphenyl bis-ylidenemalononitrile (3.34 g, 0.01 mol). Yield 3.20 g (81%), m.p. 281—283 °C. Found (%): C, 66.19; H, 3.68; N, 14.17; S, 16.21. $C_{22}H_{14}N_4S_2$. Calculated (%): C, 66.31; H, 3.54; N, 14.06; S, 16.09. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 399 $[M + H]^+$ (100). IR, ν/cm^{-1}: 3340 (N—H_{val}), 2240 (CN), 1560 (Ar), 1290 (N—H_{def}). ^1H NMR, δ: 6.51 (s, 2 H, thiophene), 7.12 (br.s, 4 H, NH_2), 7.28 (d, 4 H, Ar, J = 2.2 Hz), 7.58 (d, 4 H, Ar, J = 2.2 Hz).

4,4′-[Oxybis(4,1-phenylene)]bis(2-aminothiophene-3-carbonitrile) (3) was synthesized from 4,4′-diacetyldiphenyl oxide bis-ylidenemalononitrile (3.50 g, 0.01 mol). Yield 4.10 g (93%), m.p. 277—279 °C. Found (%): C, 63.67; H, 3.51; N, 13.44; S, 15.59. $C_{22}H_{14}N_4OS_2$. Calculated (%): C, 63.75; H, 3.40;

N, 13.52; S, 15.47. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 415 [M + H]$^+$ (100). IR, ν/cm^{-1}: 3320 (N—H$_{\mathrm{val}}$), 2220 (CN), 1530 (Ar), 1280 (N—H$_{\mathrm{def}}$), 1090 (C—O$_{\mathrm{val}}$). ^{1}H NMR, δ: 6.60 (s, 2 H, thiophene), 7.32 (br.s, 4 H, NH$_2$), 7.70 (d, 4 H, Ar , J = 2.8 Hz), 7.80 (d, 4 H, Ar , J = 2.8 Hz).

4,4′-(9*H*-Fluorene-2,7-diyl)bis(2-aminothiophene-3-carbonitrile) (4) was synthesized from 1,9-diacetylfluorene bis-ylidenemalononitrile (3.46 g, 0.01 mol). Yield 3.20 g (77%), m.p. 256—258 °C. Found (%): C, 67.19; H, 3.59; N, 13.59; S, 16.77. $C_{23}H_{14}N_4S_2$. Calculated (%): C, 67.29; H, 3.44; N, 13.65; S, 15.62. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 411 [M + H]$^+$ (100). IR, ν/cm^{-1}: 3330 (N—H$_{\mathrm{val}}$), 2925 (CH$_{2(\mathrm{val})}$), 2220 (CN), 1540 (Ar), 1370 (CH$_{2(\mathrm{def})}$), 1280 (N—H$_{\mathrm{def}}$). ^{1}H NMR, δ: 4.09 (s, 2 H, CH$_2$), 6.60 (s, 2 H, thiophene), 7.30 (br.s, 4 H, NH$_2$), 7.97 (s, 2 H, Ar), 8.13 (d, 4 H, Ar, J = 2.6 Hz).

Synthesis of polyazomethines 5—8 bearing ferrocene and nitrile-thiophene groups (general procedure). A mixture of 1,1′-diacetylferrocene (1.5 mmol), the appropriate arylenebis(2-aminothiophene-3-carbonitrile) (1.5 mmol), and toluene (20 mL) was refluxed with a Dean—Stark trap for 1 h to remove water. The reaction mixture was cooled, the polymer was collected by filtration, washed with toluene, and purified by liquid—solid extraction with acetone using a Soxhlet apparatus.

Polymer 5 was synthesized from monomer **1** (0.483 g, 1.5 mmol) and 1,1′-diacetylferrocene (0.405 g, 1.5 mmol). Yield 0.74 g (89%), $\eta_{\log}$ = 0.12 dL g^{-1}, temperature at which 5% loss of the sample weight occur T_{d5} = 340 °C. IR, ν/cm^{-1}: 690 (N—H), 1390 (C—N), 1560 (Ar), 1735 (C=O of terminal groups), 2240 (CN), 3340 (N—H).

Polymer 6 was synthesized from monomer **2** (0.483 g, 1.5 mmol) and 1,1′-diacetylferrocene (0.405 g, 1.5 mmol). Yield 0.88 g (93%), $\eta_{\log}$ = 0.11 dL g^{-1}, T_{d5} = 350 °C. IR, ν/cm^{-1}: 700 (N—H), 1390 (C—N$_{\mathrm{amide}}$), 1560 (Ar), 1730 (C=O of terminal groups), 2230 (CN), 3340 (N—H).

Polymer 7 was synthesized from monomer **3** (0.621 g, 1.5 mmol) and 1,1′-diacetylferrocene (0.405 g, 1.5 mmol). Yield 0.9 g (92%), $\eta_{\log}$ = 0.17 dL g^{-1}, T_{d5} = 320 °C. IR, ν/cm^{-1}: 680 (N—H), 1380 (C—N), 1560 (Ar), 1735 (C=O of terminal groups), 2240, 3340 (N—H).

Polymer 8 was synthesized from monomer **4** (0.621 g, 1.5 mmol) and 1,1′-diacetylferrocene (0.405 g, 1.5 mmol). Yield 0.9 g (93%), $\eta_{\log}$ = = 0.18 dL g^{-1}, T_{d5} = 300 °C. IR, ν/cm^{-1}: 690 (N—H), 1390 (C—N), 1560 (Ar), 1735 (C=O of terminal groups), 2220, 3360 (N—H).

NMR spectra were recorded and elemental analyses were performed using financial support from the Ministry of Science and Higher Education of the Russian Federation on the equipment of the Center for Molecule Composition Studies of INEOS RAS.

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