DOI: 10.1002/chem.200900348

Synthesis of 2-(Selenophen-2-yl)pyrroles and Their Electropolymerization to Electrochromic Nanofilms

Boris A. Trofimov,*[a] Elena Yu. Schmidt,[a] Albina I. Mikhaleva,[a] Cristina Pozo-Gonzalo,[b] Jose A. Pomposo,[b] Maitane Salsamendi,[b] Nadezhda I. Protzuk,[a] Nadezhda V. Zorina,[a] Andrey V. Afonin,[a] Alexander V. Vashchenko,[a] Ekaterina P. Levanova,[a] and Galina G. Levkovskaya[a]

Abstract: The divergent syntheses of 2-(selenophen-2-yl)pyrroles and their *N*-vinyl derivatives from available 2-acylselenophenes and acetylenes in a one-pot procedure make these exotic heterocyclic ensembles accessible. Now we face a potentially vast area for exploration with a great diversity of far-reaching consequences including conducting electrochromic polymers with repeating of pyrrole and selenophene units (emerging rivalry for polypyrroles and polyselenophenes), the synthesis of functionalized pyrrole–selenophene assembles for advanced materials, biochemistry and medicine, exciting models for theory of polymer conductivity.

Keywords: acetylenes · electrochromic nanofilms · electropolymerization · polypyrroles · polyselenophenes

Introduction

Selenophenyl pyrroles represent appealing molecules for wide circles of chemists, theoreticians, physicists, and biochemists. Of special interest are the issues of electron communication between the heteroaromatic moieties, both in the monomers and their conjugated polymers, as well as their potential for the synthesis of electrochromic materials, fluorescent sensors, and pharmaceuticals. While polypyrroles and polythiophenes have been extensively studied[1] and have found a plethora of applications,[2] conjugated polymers with regularly alternating pyrrole and thiophene units have attracted attention only very recently.[3,4] Thus, polythienylpyrrole nanofilms have been found to exhibit potentially useful electrochromic properties.[3,5] Much less is known about polyselenophenes, although attempts have recently been made to use them in place of polythiophene in optoelectronics, for example, in solar cells.[6–8] It has been reported that regioregular poly(3-hexylselenophene) possesses a smaller optical gap (1.6 eV) in comparison with its polythiophene analogue (1.9 eV) while maintaining the same HOMO level (4.8 eV).[9] Despite the efforts that have been made to date, polyselenophenes remain little understood and only a limited number of selenophene-based monomers have hitherto been polymerized to give materials for LEDs and solar cell devices.[7,10] Besides, the potential of selenophene as a constituent unit of conducting polyconjugated systems, and in particular the role of the selenium atom in affecting the conductivity, is still unclear.[6] Nevertheless, polymers synthesized from selenophene-tailored monomers are considered to be promising materials for NIR-active electrochromic devices.[8] A novel selenophene-based polymer with an optical contrast ($\Delta\%$ T) of 35% at 1240 nm has been described.[8] 2,6-Diphenylbenzo[1,2-*b*:4,5-*b*′]diselenophenes have been shown to be high-performance semiconductors for organic field-effect transistors.[11] Hexyl-substituted oligoselenophenes with central tetrafluorophenylene units have also been synthesized for this application.[12]

[a] Prof. Dr. B. A. Trofimov, Dr. E. Yu. Schmidt, Prof. Dr. A. I. Mikhaleva, Dr. N. I. Protzuk, Dr. N. V. Zorina, Dr. A. V. Afonin, Dr. A. V. Vashchenko, Dr. E. P. Levanova, Prof. Dr. G. G. Levkovskaya
A. E. Favorsky Irkutsk Institute of Chemistry
Siberian Branch of the Russian Academy of Sciences
1 Favorsky Str., 664033 Irkutsk (Russian Federation)
Fax: (+7) 3952-41-93-46
E-mail: boris_trofimov@irioch.irk.ru

[b] C. Pozo-Gonzalo, J. A. Pomposo, M. Salsamendi
New Materials Department
CIDETEC—Centre for Electrochemical Technologies
Paseo Miramón 196, 20009 Donostia-San Sebastián (Spain)

Among the most extensively investigated materials for organic thin-film transistors are selenophene-based heteroacenes.[13] Recently, electrosyntheses of free-standing, highly conducting polyselenophene films in an ionic liquid have been reported.[14] Selenocirculenes have been identified as a new type of semiconductors.[15]

Therefore, the synthesis of new selenophene-based monomers and their chemical modification is an area of increasing interest. For example, selenophene analogues of ethylenedioxythiophene and its polymer, polyethylenedioxythiophene (PEDOT), one of the most versatile organic conductors, have been synthesized.[16] In this context, selenophene–pyrrole ensembles might be prospective monomers for the synthesis of novel conducting materials for optoelectronic applications. However, such ensembles, particularly 2-(selenophen-2-yl)pyrroles, which provide a better conjugated chain when polymerized, are practically inaccessible. To the best of our knowledge, prior to this work, only a few representatives of this series, including 2-(selenophen-2-yl)pyrrole and its *N*-vinyl derivative, were known. These monomers were synthesized from the oxime of 2-acetylselenophene and acetylene (Trofimov reaction[17]) under atmospheric pressure (KOH/DMSO, 95–97 °C, 5 h) in low yields (10 and 2%, respectively).[18] 2-(1-Methylselenophen-2-yl)pyrrole has been claimed to be employed in the synthesis of electroactive polymers exhibiting high quantum efficiency, good colour purity, and long-term stability, which were therefore deemed useful for application in photoelectric devices, for example, high-resolution full-colour displays.[19] Also, in a patent,[20] 2-(2-selenophenyl)-1-substituted pyrroles were mentioned among other selenophene-containing compounds possessing antitumour activity.

The main goal of this work has been to develop a divergent synthesis of 2-(selenophen-2-yl)pyrroles to pave the way to novel families of conducting polymers with alternation of selenophene and pyrrole moieties, which may then constitute new types of electrochromic materials, fluorophores, pharmaceuticals, and synthetic building blocks, thus forging a link between selenophene and pyrrole chemistries. A further goal of this work has been a preliminary study on the electrochemical behaviour of the above monomers and electrogenerated polymers and their electrochromic properties. To reach these goals we have elaborated a novel, more efficient synthesis of 2-(selenophen-2-yl)pyrroles that differs from the known strategy[18] in that it employs compressed acetylene.

We report here the important details of the synthesis and electropolymerization of 2-(selenophen-2-yl)pyrroles, as well as the primary properties of their polymers.

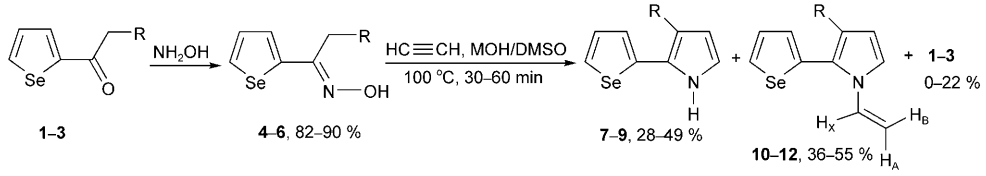
Results and Discussion

2-(Selenophen-2-yl)pyrroles **7**–**9** and their vinyl derivatives **10**–**12** have been synthesized from acylselenophenes **1**–**3** (through their oximes **4**–**6**) and acetylene. The reactions were carried out in the presence of MOH/DMSO systems (M = Na, K) under acetylene pressure (autoclave) at 100 °C for 30–60 min. The yields amounted to 49% (for pyrroles **7**–**9**) and 55% (for 1-vinylpyrroles **10**–**12**; Scheme 1).

The initial acetylene pressure at ambient temperature was 14 atm and the maximum pressure at the reaction temperature reached 25 atm. The high-pressure synthesis thus developed possesses substantial advantages. First of all, it ensures good isolated yields of both 1*H*- and 1-vinylpyrroles (of the order of 50%) and the complete conversion of oximes **4**–**6**, that is, it is acceptable for large-scale processing whereas the former protocol only allowed the compounds **7** and **10** to be obtained in very low yields (10 and 2%, respectively, based on the oxime consumed), the conversion of the starting oxime **4** being 45%. It is for this reason that pyrroles **7** and **10** have hitherto been only scantily characterized (^{1}H and ^{13}C NMR for **7** and ^{1}H NMR only for **10**). Another clear benefit of our novel method is that the reaction takes a much shorter time to reach completion (30–60 min instead of 5 h). Besides, the MOH content in the reaction mixture was only half of that used previously, and for the synthesis of 2-(selenophen-2-yl)pyrroles **7**–**9** KOH could be replaced by NaOH (a milder base).

Besides the target 1*H*-pyrroles **7**–**9** and 1-vinylpyrroles **10**–**12**, the crude product contained 0–22% of the ketones **1**–**3** originating from deoximation of the initial oximes **4**–**6**. Since ketones **1**–**3** can be easily converted back to the starting oximes, the actual yields of pyrroles **7**–**12** calculated for the reacted oximes were even higher than those shown in Scheme 1.

Representative yields and the structure/product ratio relationships are given in Table 1. As mentioned above, the crude product was composed of a mixture of 1*H*-pyrroles, 1-vinylpyrroles (major components), and minor amounts of ketones **1**–**3**, these components being easily separated by column chromatography (Al_2O_3). As can be seen from Table 1, the use of NaOH allowed 1*H*-pyrroles **7**–**9** to be



Scheme 1. Synthesis of oximes of 2-acylselenophenes **4**–**6**, 2-(selenophen-2-yl)pyrroles **7**–**9**, and 2-(selenophen-2-yl)-1-vinylpyrroles **10**–**12**; R = H: **1**, **4**, **7**, **10**; R = Me: **2**, **5**, **8**, **11**; R = Et: **3**, **6**, **9**, **12**.

synthesized preferentially, while KOH promoted their further vinylation to 1-vinylpyrroles **10–12**. In special cases (R = Me, KOH, 30 min), the reaction proceeded chemoselectively to furnish exclusively 1-vinylpyrroles (e.g., **11**) in 50% yield (Table 1).

Table 1. Influence of conditions on the yields and ratio of the reaction products (Scheme 1, 100 °C, MOH/DMSO molar ratio 1:1).

R	M	*t* [min]	Ketone **1–3** (yield [%])	Pyrrole **7–9** (yield [%])	1-Vinylpyrrole **10–12** (yield [%])
H	Na	60	**1** (10)	**7** (28)	**10** (18)
H	K	30	**1** (18)	**7** (6)	**10** (36)
Me	Na	60	**2** (22)	**8** (42)	**11** (11)
Me	K	30	**2** (trace)	**8** (trace)	**11** (50)
Et	Na	60	**3** (2)	**9** (49)	**12** (14)
Et	K	30	**3** (trace)	**9** (8)	**12** (55)

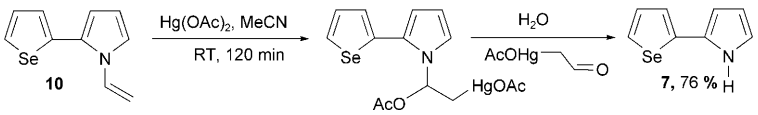
The possibility of selectively obtaining 2-(selenophen-2-yl)-1-vinylpyrroles **10–12** in one-pot and in reasonable yields (up to 55%) is a further notable benefit of this method, particularly when taking into account that 1-vinylpyrrole **10** has hitherto only been synthesized in negligible yield (2%).[18] It is worthwhile emphasizing that 1-vinylpyrroles **10–12** provide extra opportunities for functionalization of selenophene–pyrrole ensembles through subjecting them to various addition reactions to which the *N*-vinyl group is known to be so prone.[21] Of special promise would seem to be the potential ability of 2-(selenophen-2-yl)-1-vinylpyrroles to undergo vinyl polymerization, which, when coupled with oxidative dehydrocondensation, should open novel horizons for the design of electroconducting networks.

Additionally, 2-(selenophen-2-yl)-1-vinylpyrroles may be considered as protected 1*H*-pyrroles because the 1-vinyl group can be readily and cleanly removed upon treatment of 1-vinylpyrroles **10–12** with 0.5 equiv of $Hg(OAc)_2$ in aqueous MeCN (Scheme 2).

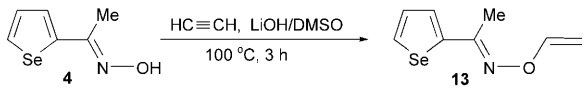
It follows that mixtures of 1*H*- and 1-vinylpyrroles, as are normally formed in this reaction, can easily be converted into 1*H*-pyrroles.

Notably, in the system LiOH/DMSO under the same conditions, no reaction of oxime **4** with acetylene occurred. When the reactants were left in contact for longer (3 h), *O*-vinyloxime **13**, the first vinylated acylselenophene oxime, was isolated as the only reaction product (yield 44%; complete conversion of oxime **4**), with ketone **1** and pyrrole **7** being detectable (GLC) in trace amounts (Scheme 3).

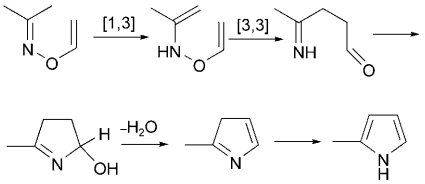
O-Vinylketoximes have been shown to be precursors of 1*H*-pyrroles,[17] being capable of rearranging according to Scheme 4.



Scheme 2. Deprotection of 2-(selenophen-2-yl)-1-vinylpyrrole.

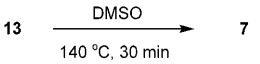


Scheme 3. Synthesis of *O*-vinyloxime **13**.



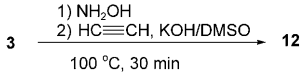
Scheme 4. Mechanism of the rearrangement of *O*-vinyloximes to pyrroles.

Indeed, when *O*-vinyloxime **13** was heated (140 °C, 30 min, DMSO), pyrrole **7** was formed in 87% yield (Scheme 5). Evidently, the synthesis of *O*-vinyloximes of 2-acylselenophenes in the system LiOH/DMSO, followed by their rearrangement, may be considered as an alternative methodology for the selective preparation of 2-(selenophen-2-yl)-1*H*-pyrroles.



Scheme 5. Selective synthesis of 2-(selenophen-2-yl)pyrroles **7** from *O*-vinyloximes of 2-acylselenophenes **13**.

A straightforward transformation of 2-acylselenophenes to 2-(selenophen-2-yl)pyrroles, avoiding the separate preparation of their oximes, has also been developed, as exemplified in Scheme 6.



Scheme 6. One-pot synthesis of 2-(selenophen-2-yl)-1-vinylpyrrole **12** directly from 2-butyrylselenophene **3** and acetylene.

This novel short-cut modification allowed the realization of a selective synthesis of 2-(selenophen-2-yl)-1-vinylpyrroles in unoptimized yields of up to 39%.

The electrochemical behaviour of 2-(selenophen-2-yl)pyrroles **7–9** was represented by typical cyclic voltammograms that displayed two irreversible oxidation peaks in the regions 0.76–0.91 and 1.35–1.52 V attributable to ionization of the pyrrole and selenophene moieties, respectively (Figure 2, Table 2). This assignment was essentially based on the ionization potentials of pyrrole (8.3 eV) and selenophene (9.0 eV) moieties.[22]

The two observed oxidation potentials were significantly lower than those of the respective parent compounds: pyrrole (1.0–1.5 V)[23] and selenophene (1.8 V).[6] Similar electrochemical behaviour has been report-

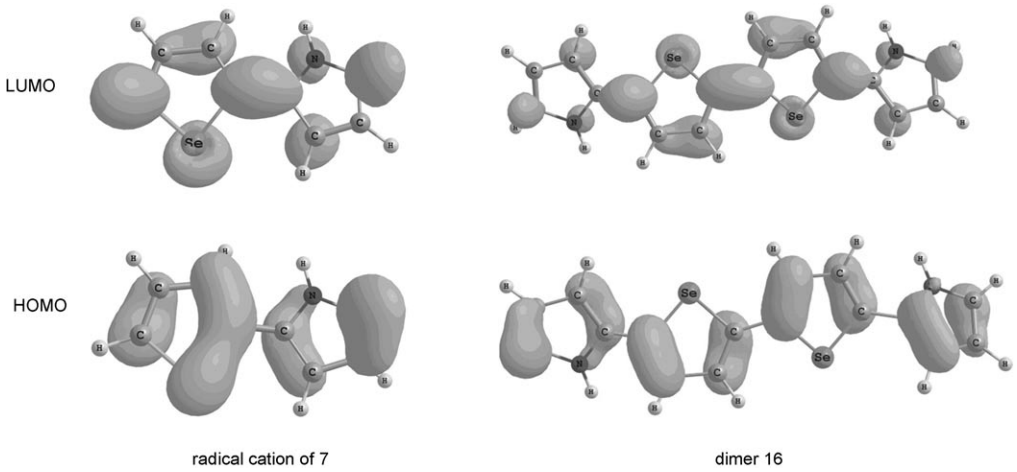


Figure 1. B3LYP/6-31G(d) frontier orbitals for the radical cation of **7** and neutral dimer **16**.

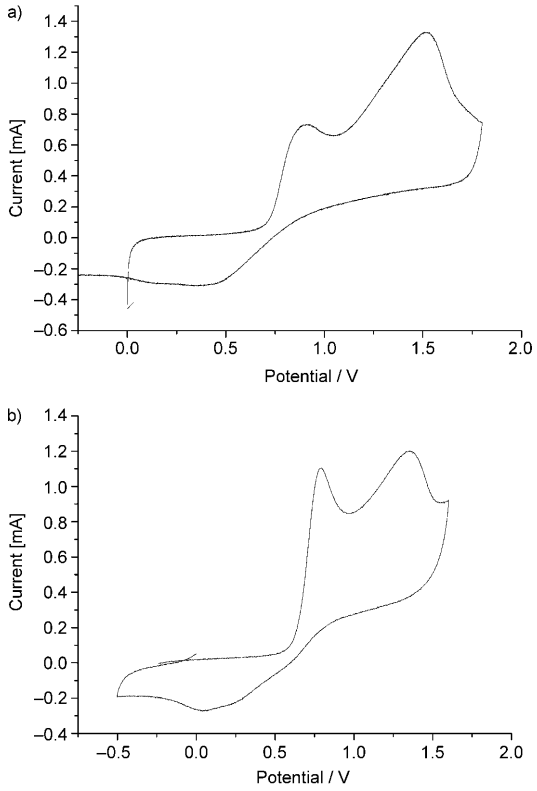


Figure 2. Cyclic voltammograms of pyrroles **7** and **9** in acetonitrile solution with 10^{-3} M substrate and 0.1 M $LiClO_4$, Pt as working and auxiliary electrodes, and Ag/AgCl as reference electrode.

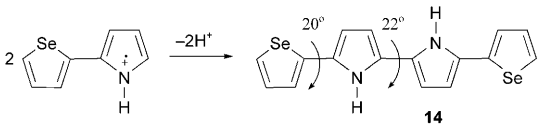
ed for 2,2-biselenophene, which was electrochemically oxidized at a much lower potential than selenophene (1.34 vs 1.8 V, *vs* Ag/AgCl).[6]

Table 2. Electrochemical behaviour of pyrroles **7–9** and the corresponding polymers poly(**7**)–poly(**9**).

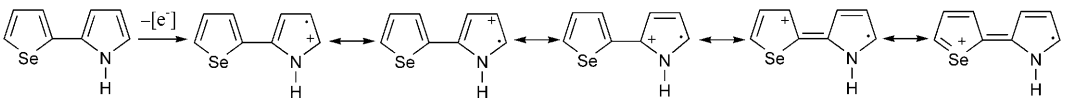
Pyrrole	**7**	**8**	**9**
Monomer			
E_{ox1} [V]	+0.91	+0.76	+0.79
E_{ox2} [V]	+1.52	+1.40	+1.35
Polymer			
E_{ox} [V]	+0.36	+0.42	+0.29

This was the anticipated result of the charge distribution in the primary radical cations generated by oxidation (Scheme 7).

Thus, the radical cation first generated in the pyrrole moiety is stabilized by a transfer of electron density from the selenophene ring, which lowers the oxidation potential. Similar stabilization (although to a greater extent due to the higher electron-donating power of the pyrrole moiety compared to that of selenophene) and hence a lowering of the oxidation potential will take place when the selenophene moiety is oxidized. Since at lower oxidation potentials (0.76–0.91 V) the positive charge and spin are mostly localized in the pyrrole ring, pyrrole–pyrrole homo-coupling with the loss of two protons should occur kinetically to give predominately dimer **14** (Scheme 8).



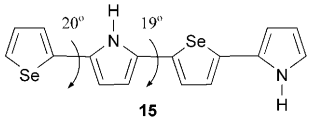
Scheme 8. The tentatively postulated initiation and first step of the electropolymerization of 2-(selenophen-2-yl)pyrroles.



Scheme 7. Participation of the selenophene moiety in stabilization of the radical cation electrogenerated in the pyrrole part of pyrrole **7**.

This scheme follows from the classic mechanism of pyrrole electropolymerization[24,25] and its quantum chemical rationalization.[25,26] Apparently, the second oxidation potential (1.35–1.52 V) corresponds to oxidation of the terminal selenophene rings, both in the dimer **14** and the subsequently formed oligomers.

Generally, two further alternative structures, **15** and **16**, may result from oxidative dimerization of 2-(selenophen-2-yl)pyrrole:



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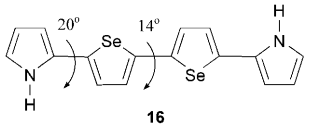

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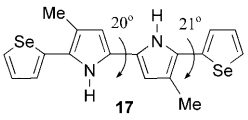
Our DFT calculations using the B3LYP functional and the 6-31G(d) basis set predict that structure **16** should be somewhat thermodynamically favourable, lying 0.9–1.0 and 1.2–1.3 kcal mol^{-1} lower in energy than structures **15** and **14**, respectively. The calculations also show that the conformers with the *trans* arrangement (relative to the heteroatom disposition) are slightly lower in energy (by about 0.5 kcal mol^{-1}) than those with the *cis* arrangement. Thus, while the above kinetic and mechanistic considerations predict pyrrole–pyrrole homo-coupling with the generation of structure **14** to be most probable, thermodynamic considerations (quantum chemical calculations) predict structure **16** (selenophene–selenophene coupling) to be more favourable. Meanwhile, further electropolymerization of both dimers (**14** and **16**) will lead to the same dipyrrole–diselenophene regioregular alternating polymeric chain, rather than one with pyrrole–selenophene alternation.

The same quantum chemical calculations predicted the torsion angles between the pyrrole and selenophene rings in monomers **7** and **8** to be 29 and 28°, respectively, with the radical cations generated from **7** and **8** being planar. In dimers **14** and **15**, the torsion angles between the heterocyclic rings were calculated at the B3LYP/6-31G(d) level to range from 19 to 22°, whereas in the thermodynamically most stable dimer **16** the torsion angle between the selenophene–selenophene rings was calculated to be remarkably lower (14°), though the angle between the pyrrole and selenophene rings remains as in the dimers **14** and **15** (20°). This planarization upon going from monomer **7** to dimers **14**–**16** is actually predictable and is a consequence of the increased conjugation. Figure 1 displays the electron density distribution in the radical cation of monomer **7** and neutral dimer **16** in terms of the HOMO and LUMO. It can be seen that the HOMOs and LUMOs in both the radical cation of **7** and neutral dimer **16** are qualitatively of the same nature (Figure 1): the HOMOs are antibonding in the region of the inter-ring bonds, while the LUMOs for this region are distinctly bonding. In dimers **14** and **15**, the electron density distributions in the HOMO and LUMO do not change substantially.

Experimentally, alkyl groups (Me, Et) at the 3-position of the pyrrole ring were found to decrease both oxidation potentials even further (from 0.91 to 0.76 V and from 1.52 to 1.35 V, Figure 2, Table 2), which is consistent with the electron-donating effects of these substituents. All of the above features were observed in relation to the electropolymerization of 3-alkyl-2-(2-thienyl)-1*H*-pyrroles.[3,5] As in the case of the thiophene analogues, the effect of 3-alkyl substituents on the electron communication between the pyrrole and selenophene moieties is of a dual nature, that is, not only electronic, but also steric. The latter effect disrupts the ring coplanarity and hence weakens the conjugation. Thus, the influence of alkyl groups in pyrroles **7**–**9** is the net effect of electron donation and displacement of the rings from coplanarity. This is in accordance with our quantum chemical calculations (using the same basis set) on the conformational structures of dimers **17**–**19** generated from monomer **8**:



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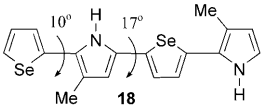

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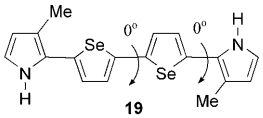

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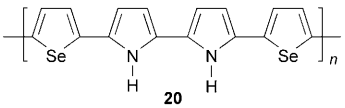
The calculated conformations are generally more planarized than those generated from unsubstituted monomer **7**, the thermodynamically most stable conformation **19** being entirely planar. Thus, in the latter case, the electron-donating effect of the methyl group, which increases the conjugation, overcomes the steric influence. It follows that the longer oligomeric or polymeric chains of poly(**7**)–poly(**9**) should preferably be planar or close to planar.

Electropolymerization of pyrroles **7**–**9** was monitored (Figure 3) during successive scans over the first oxidation potential using Pt as a working electrode. The polymerization led to the generation of polymer nanofilms on the surface with a thickness between 64 and 103 nm. The current increase after each scan indicated the electrodeposition of the polymer on the electrode. Of note here are the new oxidation waves emerging after successive scanning. These are obviously the result of conjugation enhancement along the polymeric chain, as is typically observed for conducting polymers. In view of the probable initial formation of dimer **14**, the deposited polymer is likely to have prevailing regioregular structure **20**:



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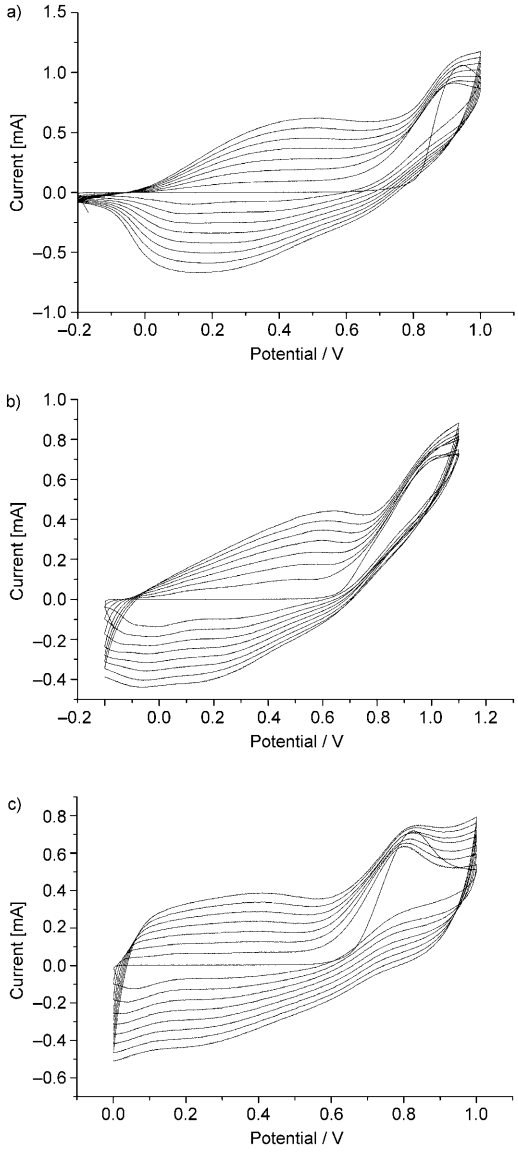

Figure 3. Electrochemical polymerization of pyrroles **7**–**9** by successive scanning over the first oxidation process in a 10^{-3} M substrate and 0.1 M $LiClO_4$ solution in acetonitrile, with Pt as working and auxiliary electrodes and Ag/AgCl as reference electrode.

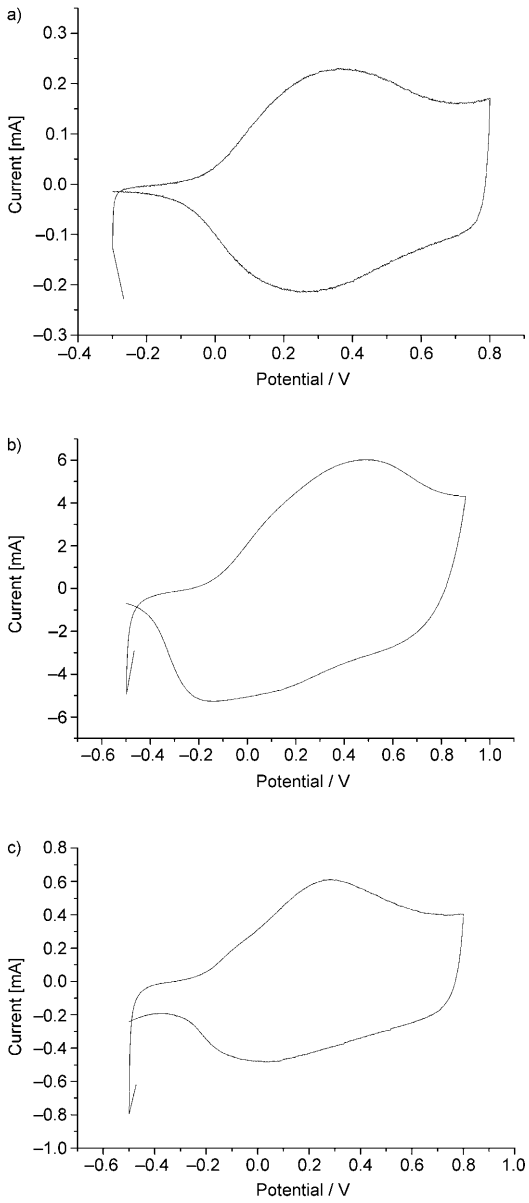

Figure 4. Cyclic voltammograms of a) poly(**7**), b) poly(**8**), and c) poly(**9**) in a monomer-free acetonitrile solution.

It is understood that pyrrole–selenophene coupling and α-β coupling may be involved in the electropolymerization, particularly during its later stages, which would disrupt the regioregular structure of the final polymer.

Figure 4 shows the electrochemical behaviour of poly(**7**)–poly(**9**) electrogenerated on Pt substrates. The polymers display one reversible oxidation peak in the range 0.29–0.42 V, a potential that is significantly lower than those for the corresponding monomers. This behaviour is consistent with the increase in conjugation length of the electrogenerated polymers poly(**7**)–poly(**9**), which lowers the oxidation potential.

Spectroelectrochemistry experiments (Figure 5, Table 3) showed that at −1 V the polymers display one absorption band in the range 445–488 nm, which is shifted by more than 100 nm compared to the corresponding bands of the monomers. This increase in wavelength relates to the extended conjugation in the polymer. Upon oxidation, the intensity of this band decreased and a new band in the range 713–745 nm emerged due to the formation of charge carriers such as polarons. After increasing the doping level, another new band appeared at 826–851 nm attributable to the formation of bipolaron states. An isosbestic point was observed for each of the polymers poly(**7**)–poly(**9**) in the range 543–579 nm.

As far as the number of bands due to polaron or bipolaron states is concerned, experimentally, when the doping level of a conducting polymer is increased, a band associated with the polaron state appears. Upon further doping, this

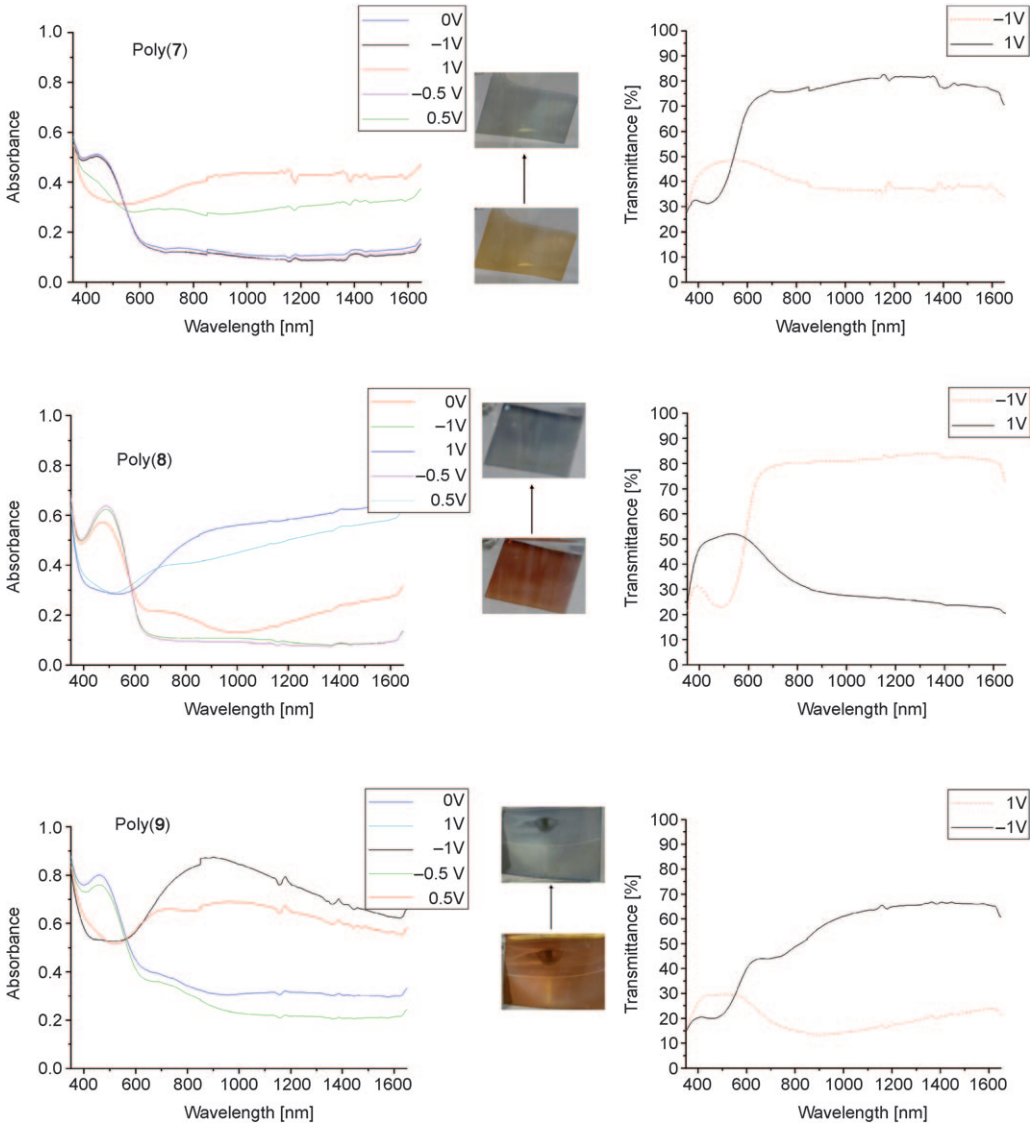

Figure 5. UV/Vis/IR spectroelectrochemistry (on the left) for poly(**7**)–poly(**9**) on indium tin oxide (ITO) plastic and the corresponding optical contrasts (on the right) for films obtained electrochemically applying the same number of scans (six cycles); Pt wire counter electrode, Ag/AgCl reference electrode, $LiClO_4$ supporting electrolyte (0.1 M).

Table 3. Absorption bands of monomers **7**–**9** and the electrogenerated poly(**7**)–poly(**9**).

	7	**8**	**9**
monomer [nm]	312	314	314
polymer [nm]	445, 713, 826	488, 745, 851	459, 718, 850

band disappears and a new band with higher wavelength due to the bipolaron emerges. This second band has been observed for each of the polymers poly(**7**)–poly(**9**). These processes have been thoroughly discussed in the literature.[27]

Poly(**7**)–poly(**9**) display dual electrochromic behaviour. In the case of the unsubstituted poly(**7**), the colour of the polymeric film switched from orange to black upon oxidation, which resembles the electrochromic behaviour of the corresponding thiophene analogue, poly[2-(2-thienyl)-1*H*-pyrrole].[3] However, after the same number of scans (six cycles), the alkyl derivatives poly(**8**) and poly(**9**) gave deeply coloured films that switched between deep-orange and greyish-blue. Similar features have been observed for the corresponding poly[2-(2-thienyl)-1*H*-pyrroles].[5] The introduction of alkyl substituents at the 3-position of the pyrrole ring strongly affects the electrochromic behaviour of the electrogenerated polymeric films of 2-(selenophen-2-yl)-pyrroles **7**–**9** (Figure 5), which is clearly due to a greater range of the conjugation alteration (because of the changes in coplanarity) during the doping–dedoping processes. The optical contrast observed for poly(**7**)–poly(**9**) lies between 13 and 26% in the visible region; however, a significant optical contrast as high as 58% has been observed in the IR region (1240 nm), indicating that these materials are likely to be very suitable for near-infrared applications. This opti-

cal contrast is higher than that reported for other selenophene-based polymers such as 1,4-di(selenophen-2-yl)benzene.[8]

Conclusion

In conclusion, a divergent general methodology for the synthesis of hitherto inaccessible 2-(selenophen-2-yl)pyrroles and their 1-vinyl derivatives from available 2-acylselenophenes and acetylene at pressures of up to 25 atm in MOH (M = Na, K)/DMSO superbasic systems has been developed. This methodology allows the selective synthesis of either 2-(selenophen-2-yl)pyrroles or 2-(selenophen-2-yl)-1-vinylpyrroles: with NaOH, the non-vinylated pyrroles are formed preferentially, while with KOH exclusively the corresponding 1-vinylpyrroles are produced. 2-(Selenophen-2-yl)pyrroles have also been shown to be selectively accessible by either facile removal of the 1-vinyl group from the corresponding 1-vinyl derivatives or by clean rearrangement of the *O*-vinyloximes of 2-acylselenophenes, the pyrrole precursors being selectively formed from oximes of 2-acylselenophenes and acetylene under pressure in the LiOH/DMSO system. 2-(Selenophen-2-yl)pyrroles have been shown to be capable of electropolymerization to afford electrochromic nanofilms displaying multi-colour switching.

These systems open up a new, unexplored, and potentially vast area of research at the interface between pyrrole and selenophene chemistries and hold promise for the design of a new generation of optoelectronic materials, selenium-containing drugs, as well as pyrrole- and selenophene-tailored building blocks.

Experimental Section

NMR spectra were recorded at RT on a Bruker DPX 400 spectrometer (^{1}H: 400.13 MHz; ^{13}C: 101.61 MHz) with HMDS as an internal standard. The peaks in the ^{1}H and ^{13}C NMR spectra were assigned with the aid of COSY, NOESY, HSQC, and HMBC experiments. IR spectra were obtained on a Bruker IFS 25 instrument.

Description of the equipment: Electrochemical characterizations were performed in a typical three-electrode set-up using an EC-Lab MPG Bio-logic multi-potentiostat employing both Pt sheet and indium tin oxide (ITO) as working electrodes, Pt sheet as counter electrode, and Ag/AgCl as reference electrode. The experiments were carried out in 10^{-3} M monomer solution in acetonitrile with 0.1 M $LiClO_4$ solution in acetonitrile as supporting electrolyte. UV/Vis measurements were made with a Jasco V-570 spectrophotometer. This UV/Vis spectrophotometer covers the range from 200 to 2500 nm. However, during spectroelectrochemistry measurements using acetonitrile as solvent, huge absorption bands of the solvent at wavelengths higher than 1600 nm were observed. This was found even when using the same solvent as a reference. For this reason, the experiments were performed only between 400 and 1600 nm.

Calculations were performed with Gaussian software (Gaussian 03W).[28]

Synthesis of ketones 1–3: Ketones **1–3** were prepared by a previously reported procedure,[29] which we have improved to increase the yields of the target compounds.

The requisite acyl chloride (46 mmol) was added portionwise to a stirred mixture of anhydrous $AlCl_3$ (6.17 g, 46 mmol) and dichloromethane (100 mL) under argon at −15 °C over a period of 0.5 h. The reaction mixture was stirred for 0.5 h and then selenophene (6.07 g, 46 mmol) was introduced dropwise over 2.5 h. The resulting mixture was allowed to warm to ambient temperature and was then stirred for a further 1 h. Thereafter, it was poured onto crushed ice and the residue in the flask was treated with water and CH_2Cl_2 until complete dissolution. The liquids were combined, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with water and dried over $MgSO_4$. After evaporation of the solvent and vacuum distillation of the residue, the respective ketones **1–3** were obtained.

2-Acetylselenophene (1): Light-yellow liquid (48%); b.p. 84–89 °C (5 mmHg); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.34 (dd, $^3J_{4,5}$ = 5.5 Hz, $^4J_{3,5}$ = 1.0 Hz, 1H; 5-H), 7.87 (dd, $^3J_{4,3}$ = 3.9 Hz, $^4J_{3,5}$ = 1.0 Hz, 1H; 3-H), 7.36 (dd, $^3J_{4,5}$ = 5.5 Hz, $^3J_{4,3}$ = 3.9 Hz, 1H; 4-H), 2.53 ppm (s, 3H; Me); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 191.61 (C=O), 151.27 (C-2), 139.90 (C-5), 134.87 (C-3), 130.61 (C-4), 25.94 ppm (Me); IR (film): $\tilde{\nu}$ = 3096, 3000, 2922, 2360, 2342, 1654, 1529, 1358, 1311, 1269, 1086, 1046, 1021, 919, 849, 801, 710, 633, 601, 557 cm^{-1}; HRMS (FAB): *m*/*z* (%) (for ^{80}Se): 174 (27.7) $[M]^+$, 159 (32.7) $[M-CH_3]^+$, 131 (11.1) $[C_4H_3Se]^+$, 105 (6.5) $[C_2HSe]^+$, 93 (2.6) $[CHSe]^+$, 80 (2.9) $[Se]^+$, 65 (2.8) $[C_5H_5]^+$, 50 (13.8) $[C_4H_2]^+$; elemental analysis calcd (%) for C_6H_6OSe (173.07): C 41.63, H 3.47, Se 45.65; found: C 41.52, H 3.49, Se 46.0.

2-Propionylselenophene (2): Light-yellow liquid (45%); b.p. 87–88 °C (2.5 mmHg); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.31 (d, $^3J_{4,5}$ = 5.3 Hz, 1H; 5-H), 7.88 (d, $^3J_{4,3}$ = 3.3 Hz, 1H; 3-H), 7.35 (dd, $^3J_{4,5}$ = 5.3 Hz, $^3J_{4,3}$ = 3.3 Hz, 1H, 4-H), 2.91 (q, ^3J = 7.3 Hz, 2H; CH_2), 1.20 ppm (t, ^3J = 7.3 Hz, 3H; Me); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 194.61 (C=O), 150.97 (C-2), 139.21 (C-5), 133.75 (C-3), 130.54 (C-4), 31.69 (CH_2), 8.51 ppm (Me); IR (film): $\tilde{\nu}$ = 3095, 2977, 2936, 2904, 2876, 1760, 1655, 1564, 1529, 1425, 1376, 1348, 1233, 1215, 1087, 1045, 928, 884, 797, 708, 651, 571 cm^{-1}; HRMS (FAB): *m*/*z* (%) (for ^{80}Se): 188 (16.4) $[M]^+$, 159 (43.7) $[M-C_2H_5]^+$, 131 (17.0) $[C_4H_3Se]^+$, 105 (9.8) $[C_2HSe]^+$, 93 (2.5) $[CHSe]^+$, 63 (1.3), 51 (9.3) $[C_4H_3]^+$; elemental analysis calcd (%) for C_7H_8OSe (187.10): C 44.95, H 4.28, Se 42.23; found: C 44.95, H 4.11, Se 42.49.

2-Butyrylselenophene (3): Light-yellow liquid (45%); b.p. 78–81 °C (1 mmHg); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.32 (dd, $^3J_{4,5}$ = 5.4 Hz, $^4J_{3,5}$ = 1.0 Hz, 1H; 5-H), 7.89 (dd, $^3J_{4,3}$ = 4.0 Hz, $^4J_{3,5}$ = 1.0 Hz, 1H; 3-H), 7.35 (dd, $^3J_{4,5}$ = 5.4 Hz, $^3J_{4,3}$ = 4.0 Hz, 1H; 4-H), 2.82 (t, ^3J = 7.5 Hz, 2H; CH_2CO), 1.74 (m, 2H; CH_2Me), 0.96 ppm (t, ^3J = 7.4 Hz, 3H; Me); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 194.35 (C=O), 151.56 (C-2), 139.52 (C-5), 134.03 (C-3), 130.69 (C-4), 40.53 (CH_2CO), 18.32 (CH_2Me), 13.83 ppm (Me); IR (film): $\tilde{\nu}$ = 3096, 3082, 2963, 2932, 2873, 1734, 1707, 1654, 1528, 1457, 1425, 1364, 1271, 1232, 1206, 1075, 1048, 930, 881, 843, 780, 708, 652, 547 cm^{-1}; HRMS (FAB): *m*/*z* (%) (for ^{80}Se): 202 (18.4) $[M]^+$, 174 (2.6) $[M-C_2H_4]^+$, 159 (50.7) $[M-C_3H_7]^+$, 131 (13.3) $[C_4H_3Se]^+$, 105 (6.1) $[C_2HSe]^+$, 93 (2.8) $[CHSe]^+$, 65 (1.2), 51 (4.9) $[C_4H_3]^+$; elemental analysis calcd (%) for $C_8H_{10}OSe$ (201.12): C 47.77, H 5.01, Se 36.29; found: C 47.89, H 5.07, Se 36.59.

Synthesis of oximes 4–6: A mixture of the respective ketone (**1–3**; 10 mmol), $H_2NOH{\cdot}HCl$ (1.39 g, 20 mmol), and NaOH (0.80 g, 20 mmol) in EtOH (10 mL) was stirred at room temperature for 8 h and then poured into water (30 mL). The crystalline precipitate was collected by filtration, washed with water, and dried in vacuo to afford oximes **4–6**.

The configurations of ketoximes **4–6** could be unambiguously assigned on the basis of the well-established effect[30] that the resonance of the carbon atom that is directly linked to the oxime fragment appears at lower frequency by 4–7 ppm in the *E* isomer than the corresponding resonance of the *Z* isomer. For this reason, the δ $^{13}CH_3$ value of 12.34 ppm in **4**, the δ $^{13}CH_2$ value of 19.51 ppm in **5**, and the δ $^{13}(\alpha\text{-}CH_2)$ value of 27.80 ppm were ascribed to the *E* isomer, whereas the signals at δ = 19.39, 26.40, and 35.06 ppm, respectively, were assigned to the *Z* isomer. The other signals in the ^{1}H and ^{13}C NMR spectra of **4–6** were straightforwardly assigned by application of COSY, NOESY, HSQC, and HMBC experiments.

1-(2-Selenophenyl)-1-ethanone oxime (4): Colourless crystals (90%); m.p. 107–108 °C; *Z*/*E* 7:3; NMR for *Z* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 9.67 (s, 1H; OH), 8.35 (dd, $^3J_{5,4}$ = 5.9 Hz, $^4J_{5,3}$ = 1.0 Hz, 1H; 5-H), 7.69 (dd, $^3J_{3,4}$ = 4.2 Hz, $^4J_{3,5}$ = 1.0 Hz, 1H; 3-H), 7.38 (dd, $^3J_{4,5}$ = 5.9 Hz,

$^3J_{3,4}$=4.2 Hz, 1H; 4-H), 2.41 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=148.99 (C=N), 137.88 (C-5), 134.66 (C-2), 131.67 (C-3), 128.00 (C-4), 19.50 ppm (Me); NMR for *E* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=9.67 (s, 1H; OH), 7.90 (dd, $^3J_{5,4}$=5.6 Hz, $^4J_{5,3}$=1.0 Hz, 1H; 5-H), 7.42 (dd, $^3J_{3,4}$=3.9 Hz, $^4J_{3,5}$=1.0 Hz, 1H; 3-H), 7.25 (dd, $^3J_{5,4}$=5.6 Hz, $^3J_{3,4}$=3.9 Hz, 1H; 4-H), 2.30 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=153.67 (C=N), 145.88 (C-2), 131.62 (C-5), 129.73 (C-4), 128.97 (C-3), 12.02 ppm (Me); IR (KBr): $\tilde{\nu}$=1646, 1612, 1426, 1368, 1290, 1231, 1093, 1035, 993, 936, 832, 794, 698, 654, 450 cm^{-1}; elemental analysis calcd (%) for C_6H_7NOSe (188.09): C 38.32, H 3.75, N 7.45, Se 41.98; found: C 38.64, H 3.78, N 7.25, Se 41.70.

1-(2-Selenophenyl)-1-propanone oxime (5): Colourless crystals (86%); m.p. 85–87°C; *Z*/*E* 6:4; NMR for *Z* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=9.50 (s, 1H; OH), 8.33 (dd, $^3J_{5,4}$=5.6 Hz, $^4J_{5,3}$=1.0 Hz, 1H; 5-H), 7.72 (dd, $^3J_{3,4}$=4.2 Hz, $^4J_{3,5}$=1.0 Hz, 1H; 3-H), 7.37 (dd, $^3J_{4,5}$=5.9 Hz, $^3J_{3,4}$=4.2 Hz, 1H; 4-H), 2.80 (q, ^3J=7.5 Hz, 2H; CH_2), 1.32 ppm (t, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=152.53 (C=N), 137.12 (C-5), 133.65 (C-2), 130.62 (C-3), 127.51 (C-4), 26.40 (CH_2), 12.02 ppm (Me); NMR for *E* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=9.50 (s, 1H; OH), 7.90 (dd, $^3J_{5,4}$=5.6 Hz, $^4J_{5,3}$=1.0 Hz, 1H; 5-H), 7.42 (dd, $^3J_{3,4}$=3.9 Hz, $^4J_{3,5}$=1.0 Hz, 1H; 3-H), 7.26 (dd, $^3J_{5,4}$=5.6 Hz, $^3J_{3,4}$=3.9 Hz, 1H; 4-H), 2.83 (q, ^3J=7.5 Hz, 2H; CH_2), 1.22 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=157.9 (C=N), 144.74 (C-2), 131.07 (C-5), 129.26 (C-4), 128.07 (C-3), 19.51 (CH_2), 10.82 ppm (Me); IR (KBr): $\tilde{\nu}$=1633, 1623, 1463, 1426, 1370, 1289, 1254, 1225, 1093, 1064, 1024, 1007, 954, 922, 936, 871, 840, 795, 712, 690, 654, 467, 450 cm^{-1}; elemental analysis calcd (%) for C_7H_9NOSe (202.11): C 41.60, H 4.49, N 6.93, Se 39.07; found: C 41.81, H 4.66, N 7.04, Se 38.88.

1-(2-Selenophenyl)-1-butanone oxime (6): Colourless crystals (82%); m.p. 57–59°C; *Z*/*E* 6:4; NMR for *Z* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=9.44 (s, 1H; OH), 8.33 (dd, $^3J_{5,4}$=5.6 Hz, $^4J_{5,3}$=1.0 Hz, 1H; 5-H), 7.70 (dd, $^3J_{3,4}$=4.2 Hz, $^4J_{3,5}$=1.0 Hz, 1H; 3-H), 7.34 (dd, $^3J_{4,5}$=5.9 Hz, $^3J_{3,4}$=4.2 Hz, 1H; 4-H), 2.74 (q, ^3J=7.5 Hz, 2H; CH_2CH$_2$), 1.75 (m, 2H; CH_2Me), 1.01 ppm (t, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=152.10 (C=N), 137.43 (C-5), 134.20 (C-2), 131.14 (C-3), 127.92 (C-4), 35.06 (*C*H$_2$CH$_2$), 20.90 (*C*H$_2$Me), 14.53 ppm (Me); NMR for *E* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=9.44 (s, 1H; OH), 7.89 (dd, $^3J_{5,4}$=5.6 Hz, $^4J_{5,3}$=1.0 Hz, 1H; 5-H), 7.37 (dd, $^3J_{3,4}$=3.9 Hz, $^4J_{3,5}$=1.0 Hz, 1H; 3-H), 7.27 (dd, $^3J_{5,4}$=5.6 Hz, $^3J_{3,4}$=3.9 Hz, 1H; 4-H), 2.75 (q, ^3J=7.5 Hz, 2H; CH_2CH$_2$), 1.69 (CH_2Me), 1.00 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=157.39 (C=N), 145.30 (C-2), 131.43 (C-5), 129.65 (C-4), 128.61 (C-3), 27.80 (*C*H$_2$CH$_2$), 19.85 (*C*H$_2$Me), 13.86 ppm (Me); IR (KBr): $\tilde{\nu}$=1654, 1599, 1453, 1423, 1308, 1270, 1079, 1043, 994, 954, 923, 839, 794, 665, 641, 454 cm^{-1}; elemental analysis calcd (%) for $C_8H_{11}NOSe$ (216.14): C 44.46, H 5.13, N 6.48, Se 36.53; found: C 44.61, H 5.11, N 6.10, Se 36.61.

Synthesis of 1*H*-pyrroles 7–9: The respective oxime (**4–6**; 2.66 mmol) and NaOH (106 mg, 2.66 mmol) were dissolved under heating (80°C) in DMSO (50 mL). The solution of sodium oximate thus obtained was placed in a 0.25 L rotating steel autoclave. The autoclave was filled with acetylene from a cylinder to a pressure of 14 atm and then the acetylene was released to remove air. The autoclave was charged with acetylene once more to the same pressure and then heated (100°C, 60 min) under rotation. The acetylene pressure peaked at 25 atm and then rapidly decreased due to the reaction of acetylene with the ketoxime. After cooling to room temperature, the remaining pressure in the autoclave was 8 atm. The reaction mixture was then diluted with a twofold volume excess of iced water, neutralized with NH_4Cl, and the resulting solution was extracted with diethyl ether (5×5 mL). The ethereal extracts were washed with cold water (3×5 mL) to remove dissolved DMSO. The ethereal solution was then dried over K_2CO_3 overnight. After evaporation of the solvent, column chromatography of the residue (basic Al_2O_3) gave pure ketones **1–3**, 1*H*-pyrroles **7–9**, and 1-vinylpyrroles **10–12**. First, 1-vinylpyrroles **10–12** were eluted with hexane, then pyrroles **7–9** and finally ketones **1–3** were eluted with the system hexane/diethyl ether (5:1). For yields, see Scheme 1.

2-(Selenophen-2-yl)pyrrole (7): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=8.34 (s, 1H; NH), 7.78 (dd, $^3J_{5',4'}$=5.5 Hz, $^4J_{5',3'}$=1.0 Hz, 1H; 5′-H), 7.21 (dd, $^3J_{3',4'}$=3.8 Hz, $^3J_{5',4'}$=5.5 Hz, 1H; 4′-H), 7.14 (dd, $^3J_{3',4'}$=3.8 Hz, $^4J_{3',5'}$=1.0 Hz, 1H; 3′-H), 6.78 (dd, $^3J_{5,4}$=2.7 Hz, $^4J_{5,3}$=1.3 Hz, 1H; 5-H), 6.37 (dd, $^3J_{3,4}$=3.6 Hz, $^4J_{3,5}$=1.3 Hz, 1H; 3-H), 6.23 ppm (dd, $^3J_{3,4}$=3.6 Hz, $^3J_{5,4}$=2.7 Hz, 1H; 4-H); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=141.47 (C-2′), 130.22 (C-4′), 127.79 (C-5′), 128.75 (C-2), 122.71 (C-3′), 118.86 (C-5), 110.26 (C-4), 107.55 ppm (C-3); IR (film): $\tilde{\nu}$=3363, 1510, 1461, 1255, 1120, 1098, 1036, 987, 886, 817, 795, 786, 727, 680, 571 cm^{-1}; elemental analysis calcd (%) for C_8H_7NSe (196.11): C 49.00, H 3.60, N 7.14, Se 40.26; found: C 49.35, H 3.32, N 7.22, Se 40.63.

3-Methyl-2-(selenophen-2-yl)pyrrole (8): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=8.10 (s, 1H; NH), 7.86 (dd, $^3J_{5',4'}$=5.6 Hz, $^4J_{5',3'}$=1.0 Hz, 1H; 5′-H), 7.27 (dd, $^3J_{3',4'}$=3.7 Hz, $^3J_{5',4'}$=5.6 Hz, 1H; 4′-H), 7.11 (dd, $^3J_{3',4'}$=3.7 Hz, $^4J_{3',5'}$=1.0 Hz, 1H; 3′-H), 7.00 (d, $^3J_{5,4}$=2.7 Hz, 1H; 5-H), 6.11 (d, $^3J_{5,4}$=2.7 Hz, 1H; 4-H), 2.26 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=140.78 (C-2′), 130.06 (C-4′), 128.33 (C-5′), 125.12 (C-2), 123.74 (C-3′), 117.50 (C-5), 117.00 (C-3), 112.41 (C-4), 12.50 ppm (Me); IR (film): $\tilde{\nu}$=3380, 1644, 1455, 1230, 1093, 844, 790, 736, 683, 519 cm^{-1}; elemental analysis calcd (%) for C_9H_9NSe (210.13): C 51.44, H 4.32, N 6.67, Se 37.58; found: C 51.34, H 4.69, N 6.58, Se 37.36.

3-Ethyl-2-(selenophen-2-yl)pyrrole (9): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=8.06 (s, 1H; NH), 7.89 (dd, $^3J_{5',4'}$=5.6 Hz, $^4J_{5',3'}$=0.8 Hz, 1H; 5′-H), 7.29 (dd, $^3J_{3',4'}$=3.7 Hz, $^3J_{5',4'}$=5.6 Hz, 1H; 4′-H), 7.13 (dd, $^3J_{3',4'}$=3.7 Hz, $^4J_{3',5'}$=0.8 Hz, 1H; 3′-H), 6.73 (d, $^3J_{5,4}$=3.0 Hz, 1H; 5-H), 6.21 (d, $^3J_{5,4}$=3.0 Hz, 1H; 4-H), 2.69 (q, ^3J=7.6 Hz, 2H; CH_2), 1.28 ppm (t, ^3J=7.6 Hz, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=140.21 (C-2′), 129.73 (C-4′), 128.16 (C-5′), 123.79 (C-2), 123.52 (C-3′), 123.40 (C-3), 117.39 (C-5), 109.56 (C-4), 19.59 (CH_2), 14.75 ppm (Me); IR (film): $\tilde{\nu}$=3380, 2963, 2928, 2868, 1644, 1525, 1457, 1378, 1229, 1101, 990, 916, 893, 830, 786, 689 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{11}NSe$ (224.16): C 53.58, H 4.95, N 6.25, Se 35.22; found: C 53.61, H 4.95, N 6.22, Se 34.99.

Synthesis of 1-vinylpyrroles 10–12: The respective oximes (**4–6**; 2.66 mmol) and KOH·0.5 H_2O (173 mg, 2.66 mmol) were dissolved under heating (80°C) in DMSO (50 mL). The solution of potassium oximate was placed in a 0.25 L rotating steel autoclave. The autoclave was filled with acetylene from a cylinder to a pressure of 14 atm and then the acetylene was released to remove air. The autoclave was charged once more with acetylene to the same pressure and heated (100°C, 30 min) under rotation. After treatment of the reaction mixture as described above, pure **10–12** were obtained. For yields, see Scheme 1.

2-(Selenophen-2-yl)-1-vinylpyrrole (10): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=7.98 (dd, $^3J_{5',4'}$=5.6 Hz, $^4J_{5',3'}$=1.0 Hz, 1H; 5′-H), 7.30 (dd, $^3J_{3',4'}$=3.9 Hz, $^3J_{5',4'}$=5.6 Hz, 1H; 4′-H), 7.12 (dd, $^3J_{3',4'}$=3.9 Hz, $^4J_{3',5'}$=1.0 Hz, 1H; 3′-H), 7.09 (dd, $^3J_{5,4}$=3.1 Hz, $^4J_{5,3}$=1.7 Hz, 1H; 5-H), 7.08 (dd, $^3J_{BX}$=15.7 Hz, $^3J_{AX}$=8.8 Hz, 1H; H_X), 6.32 (dd, $^3J_{3,4}$=3.7 Hz, $^4J_{5,3}$=1.7 Hz, 1H; 3-H), 6.25 (dd, $^3J_{3,4}$=3.7 Hz, $^3J_{5,4}$=3.1 Hz, 1H; 4-H), 5.18 (dd, $^3J_{BX}$=15.7 Hz, $^2J_{AB}$=1.1 Hz, 1H; H_B), 4.74 ppm (dd, $^3J_{AX}$=8.8 Hz, $^2J_{AB}$=1.1 Hz, 1H; H_A); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=138.95 (C-2′), 131.50 (C-α), 131.08 (C-5′), 129.89 (C-4′), 128.79 (C-2), 128.77 (C-3′), 118.64 (C-5), 111.62 (C-3), 110.29 (C-4), 99.53 ppm (C-β); IR (film): $\tilde{\nu}$=3420, 2923, 1642, 1468, 1438, 1348, 1286, 1256, 1215, 1033, 989, 886, 812, 784, 718, 682, 582 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_9NSe$ (222.15): C 54.07, H 4.08, N 6.31, Se 35.54; found: C 54.19, H 4.09, N 6.42, Se 35.33.

3-Methyl-2-(selenophen-2-yl)-1-vinylpyrrole (11): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=8.10 (dd, $^3J_{5',4'}$=5.6 Hz, $^4J_{5',3'}$=1.1 Hz, 1H; 5′-H), 7.32 (dd, $^3J_{3',4'}$=3.7 Hz, $^3J_{5',4'}$=5.6 Hz, 1H; 4′-H), 7.10 (dd, $^3J_{3',4'}$=3.7 Hz, $^4J_{3',5'}$=1.1 Hz, 1H; 3′-H), 7.03 (d, $^3J_{5,4}$=3.1 Hz, 1H; 5-H), 6.96 (dd, $^3J_{BX}$=15.7 Hz, $^3J_{AX}$=8.9 Hz, 1H; H_X), 6.13 (d, $^3J_{5,4}$=3.1 Hz, 1H; 4-H), 5.06 (dd, $^3J_{BX}$=15.7 Hz, $^2J_{AB}$=1.1 Hz, 1H; H_B), 4.58 (dd, $^3J_{AX}$=8.9 Hz, $^2J_{AB}$=1.1 Hz, 1H; H_A), 2.08 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): δ=137.90 (C-2′), 132.71 (C-5′), 131.68 (C-α), 131.30 (C-3′), 129.59 (C-4′), 125.13 (C-2), 120.46 (C-3), 117.02 (C-5), 111.95 (C-4), 97.52 (C-β), 12.15 ppm (Me); IR (film): $\tilde{\nu}$=2964, 2918, 2850, 1639, 1475, 1452, 1388, 1369, 1330, 1305, 1297, 1229, 1186, 1080, 1009, 963, 911, 859, 836, 813, 788, 723, 688, 666, 624, 591, 458 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{11}NSe$ (236.18): C 55.94, H 4.69, N 5.93, Se 33.43; found: C 56.12, H 4.69, N 5.69, Se 33.28.

3-Ethyl-2-(selenophen-2-yl)-1-vinylpyrrole (12): Oil; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 8.07$ (dd, $^3J_{5',4'} = 5.6$ Hz, $^4J_{3',5'} = 1.0$ Hz, 1H; 5′-H), 7.29 (dd, $^3J_{3',4'} = 3.7$ Hz, $^3J_{5',4'} = 5.6$ Hz, 1H; 4′-H), 7.09 (dd, $^3J_{3',4'} = 3.7$ Hz, $^4J_{3',5'} = 1.0$ Hz, 1H; 3′-H), 7.03 (d, $^3J_{3,4} = 2.9$ Hz, 1H; 5-H), 6.87 (dd, $^3J_{BX} = 15.6$ Hz, $^3J_{AX} = 8.8$ Hz, 1H; H_X), 6.17 (d, $^3J_{3,4} = 2.9$ Hz, 1H; 4-H), 5.04 (dd, $^3J_{BX} = 15.6$ Hz, $^2J_{AB} = 1.1$ Hz, 1H; H_B), 4.56 (dd, $^3J_{AX} = 8.8$ Hz, $^2J_{AB} = 1.1$ Hz, 1H; H_A), 2.45 (q, $^3J = 7.6$ Hz, 2H; CH_2), 1.11 ppm (t, $^3J = 7.6$ Hz, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): $\delta = 137.89$ (C-2′), 132.95 (C-5′), 131.59 (C-α), 131.59 (C-3′), 129.57 (C-4′), 127.56 (C-3), 124.20 (C-2), 117.17 (C-5), 110.21 (C-4), 97.45 (C-β), 19.76 (CH_2), 15.71 ppm (Me); IR (film): $\tilde{\nu} = 2962$, 2928, 1639, 1475, 1453, 1381, 1333, 1302, 1264, 1227, 1179, 1081, 963, 907, 860, 839, 813, 788, 685 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{13}NSe$ (250.20): C 57.61, H 5.24, N 5.60, Se 31.56; found: C 57.68, H 5.26, N 5.51, Se 31.76.

Synthesis of *O*-vinyloxime 13: 1-(Selenophen-2-yl)-1-ethanone oxime **4** (500 mg, 2.66 mmol) and LiOH (64 mg, 2.66 mmol) were dissolved under heating (80 °C) in DMSO (50 mL). The solution of lithium oximate was placed in a 0.25 L rotating steel autoclave. The autoclave was filled with acetylene from a cylinder to a pressure of 14 atm and then the acetylene was released to remove air. The autoclave was charged with acetylene once more to the same pressure and heated (100 °C, 3 h) under rotation. After analogous treatment as above (except for the eluting with hexane), 250 mg (yield 44 %) of pure *O*-vinyloxime **13** was isolated.

1-(Selenophen-2-yl)-1-ethanone *O*-vinyloxime (13): Light-yellow liquid; $[n]_D^{20} = 1.5009$; *Z*/*E* 10:1; ^{1}H NMR for *Z* isomer: $\delta = 8.33$ (dd, $^3J_{5,4} = 5.6$ Hz, $^4J_{5,3} = 1.0$ Hz, 1H; 5-H), 7.67 (dd, $^3J_{3,4} = 4.0$ Hz, $^4J_{3,4} = 1.0$ Hz, 1H; 3-H), 7.35 (dd, $^3J_{4,5} = 5.6$ Hz, $^3J_{3,4} = 4.0$ Hz, 1H; 4-H), 6.99 (dd, $^3J_{BX} = 14.1$ Hz, $^3J_{AX} = 6.4$ Hz, 1H; H-X), 4.77 (dd, $^3J_{BX} = 14.1$ Hz, $^2J_{AB} = 1.3$ Hz, 1H; H-B), 4.24 (dd, $^3J_{AX} = 6.4$ Hz, $^2J_{AB} = 1.3$ Hz, 1H; H-A), 2.38 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): $\delta = 151.71$ (C-α), 150.51 (C=N), 138.07 (C-5), 134.81 (C-2), 132.45 (C-3), 128.18 (C-4), 89.27 (C-β), 19.44 ppm (Me); NMR for *E* isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.94$ (dd, $^3J_{5,4} = 5.6$ Hz, $^4J_{5,3} = 1.0$ Hz, 1H; 5-H), 7.45 (dd, $^3J_{3,4} = 4.0$ Hz, $^4J_{3,5} = 1.0$ Hz, 1H; 3-H), 7.26 (dd, $^3J_{5,4} = 5.6$ Hz, $^3J_{3,4} = 4.0$ Hz, 1H; 4-H), 6.94 (dd, $^3J_{BX} = 14.1$ Hz, $^3J_{AX} = 6.4$ Hz, 1H; H-X), 4.66 (dd, $^3J_{BX} = 14.1$ Hz, $^2J_{AB} = 1.3$ Hz, 1H; H-B), 4.16 (dd, $^3J_{AX} = 6.4$ Hz, $^2J_{AB} = 1.3$ Hz, 1H; H-A), 2.31 ppm (s, 3H; Me); ^{13}C NMR (100.69 MHz, $CDCl_3$): $\delta = 152.51$ (C=N), 152.10 (C-β), 146.08 (C-2), 132.61 (C-5), 129.81 (C-4), 129.59 (C-3), 88.39 (C-β), 12.02 ppm (Me); IR (film): $\tilde{\nu} = 3069$, 2925, 2244, 1367, 1592, 1432, 1379, 1297, 1235, 1172, 1009, 954, 901, 841, 732, 702, 652, 605 cm^{-1}; elemental analysis calcd (%) for C_8H_9NOSe (214.13): C 44.87, H 4.24, N 6.54, Se 36.88; found: C 45.05, H 4.36, N 6.47, Se 36.69.

Acknowledgements

This work has been carried out under financial support of leading scientific schools by the President of the Russian Federation (Grant NSH-263.2008.3) and the Russian Foundation for Basic Research (Grant 08-03-00002).

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Received: February 9, 2009
Published online: May 22, 2009

