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Facile synthesis and characterization of new polymerizable conjugated 2,5-di(selenophen-2-yl)pyrroles and 2,5-difuranylpyrroles

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ABSTRACT

A facile synthesis of novel π-conjugated 2,5-di(selenophen-2-yl)pyrroles (SeNSe) and 2,5-difuranylpyrroles (ONO) via Paal–Knorr reaction as the key step is presented. Photophysical and electrochemical studies of the various products have been explored. A bathochromic shift of the emission maximum is observed for all SeNSes over ONOs. Extended conjugation with a phenyl moiety further promotes the bathochromic shift. These SeNSe and ONO derivatives exhibit lower oxidation potentials than their terselenophene and terthiophene analogues.

Heterocycles possessing oxygen, sulfur and selenium atoms (group VI elements) play significant roles in the field of materials chemistry.[1] Over the past few years, significant attention has been focused on π-conjugated heterocyclic organic molecules (oligomers/polymers) due to their wide range of applications such as, organic light-emitting diodes (OLEDs),[2] nonlinear optics (NLOs),[3] field-effect transistors (FETs),[4] electrochromic devices[5] and sensor materials,[6] which are useful in display technology and data storage. In this connection, the design, synthesis and photophysical studies of π-conjugated monomer **1**, (SNS, Fig. 1) and analogues derived from group VI elements represent a field of enormous growth in materials chemistry. Conjugated oligomers/polymers, which are obtained from these derivatives provide highly conducting properties, and particularly, a range of optical properties with electronic band gaps, making them useful for numerous electrochemical applications. However, the lack of research on these derivatives is due to the poor availability of suitable synthetic methodologies for the preparation of substituted monomeric precursors.

Ferraris and Skiles first proposed the use of poly-2,5-dithienylpyrrole (poly-SNS) en route to well-defined polymers in 1987.[7] In addition, Johannsen and co-workers reported the synthesis of a series of electropolymerizable 2,5-SNS derivatives towards conductive polymers.[8] The electropolymerizable thienyl pyrrole derivatives have also been studied by different groups for electrochromic applications.[9] Moreover, soluble conducting polymers based on 2,5-dithienylpyrrole derivatives and a multi-chromic co-polymer with 3,4-ethylenedioxy thiophene (EDOT) were reported by Yildiz et al.[10] The functionalization of 2,5-dithienylpyrroles with tetracyanoethylene (TCNE) was reported by two different groups for organic field-effect transistors (OFETs).[11] Despite the many Letters published on thienyl oligomers, very little is known on their close analogues, di(selenophen-2-yl)pyrroles and difuranylpyrroles. The exciting photophysical and spectroelectrochemical properties of conducting oligomers based on 2,5-SNS derivatives, along with our ongoing interest in the synthesis of functional molecules,[12] prompted us to research 2,5-di(selenophen-2-yl)pyrroles **2**, (SeNSe) and 2,5-difuranylpyrrole derivatives **3**, (ONO). Herein, we report the first synthesis of these derivatives and present their photophysical and electrochemical properties.

The pyrrole derivatives **2** and **3** were chosen as polymer precursors for the following reasons: (i) synthesis using the Paal–Knorr reaction represents an attractive one-step procedure, (ii) the oxidation potential of SeNSe derivatives and ONO derivatives are lower (about +0.8 V vs SCE and +0.68 V vs SCE) than those of their terselenophene and terthiophene analogues (about +0.88 V vs SCE and +0.95 V vs SCE) and (iii) good quality films of poly SeNSe as well

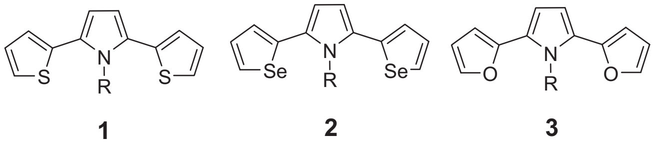

Figure 1. Conjugated pyrrole derivatives **1**, (SNS), **2**, (SeNSe), and **3**, (ONO).

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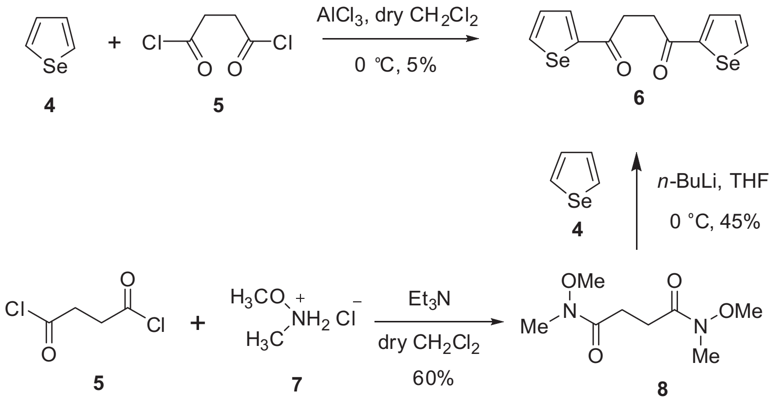
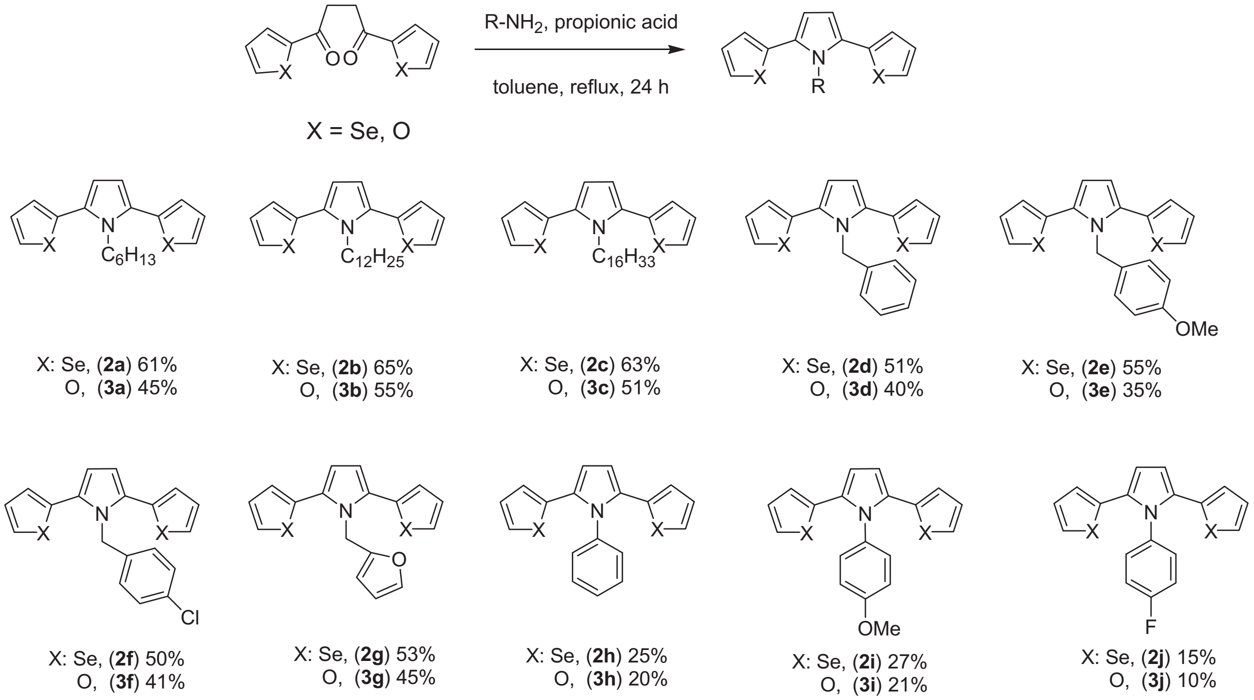
as poly ONO can be generated easily on a platinum disc working electrode.

We envisaged that the synthesis of the pyrrole derivatives **2** and **3** could be achieved via Paal–Knorr reaction with a key diketone intermediate and a wide range of aliphatic and aromatic amines. Therefore, our efforts to synthesize the pyrrole derivatives **2** and **3** started with judicious choice of the diketone **6**. As shown in Scheme 1, we initially studied the conventional double Friedel–Crafts acylation protocol where selenophene **4** and succinyl chloride **5** were reacted in the presence of a Lewis acid ($AlCl_3$). However, this transformation was rather sluggish affording a very poor yield (5%) of the desired diketone **6**. Alternatively, the use of the Weinreb amide precursor **8** (N^1,N^4-dimethoxy-N^1,N^4-dimethylsuccinamide) led to the desired diketone **6**, in a much better yield (45%). Similarly, a previously reported synthetic protocol was implemented to synthesize 1,4-di(furan-2-yl)butane-1,4-dione, which is an important intermediate for the synthesis of 2,5-difuranylpyrroles.[13]

With the diketone **6** in hand, we next investigated its cyclization with different amines. Various acid catalysts, such as propionic acid, *p*-toluenesulfonic acid (PTSA) and titanium tetrachloride were reported previously to promote cyclization to afford dithienylpyrrole derivatives.[14–16] However, it is highly important to maintain the reaction medium (solvent) at an appropriate acidity in order to avoid the formation of by-products. Hence, we carried out carefully optimization reactions to fine-tune cyclization of the diketone with primary amines by employing different solvents and catalysts. Preliminary screening results are summarized in Table S1 (Supplementary data). Initially, we used the aliphatic amines *n*-hexylamine, *n*-dodecylamine and *n*-hexadecylamine, and different solvents and acid catalysts for SeNSe (**2**) and ONO (**3**) monomer derivatives. From Table S1, it is evident that the yields of SeNSe (**2**)



Scheme 1. Synthesis of 1,4-di(selenophen-2-yl)butane-1,4-dione (**6**) via double Friedel–Crafts acylation from succinyl chloride or the corresponding double Weinreb amide.



Scheme 2. Synthesis of 2,5-di(selenophen-2-yl)pyrroles **2**, (SeNSe) and 2,5-difuranylpyrroles **3**, (ONO). X = Se (**2a–2j**) 2,5-diselenylpyrroles, X = O (**3a–3j**); 2,5-difuranylpyrroles, C_6H_{13}: *n*-hexylamine; $C_{12}H_{25}$: *n*-dodecylamine; $C_{16}H_{33}$: *n*-hexadecylamine.

and ONO (**3**) products were not high enough when benzene was employed as the solvent. Similarly, the product yields were found to be low when strong acid catalysts, such as PTSA were used, especially in the case of aliphatic or less conjugated amines. However, when a weak acid such as propionic acid was utilized, the yields increased compared to other acids. Among the other solvents tested, toluene was the best in terms of reactivity and yields. From the above investigations, toluene in the presence of propionic acid was established as optimized reaction conditions for the Paal–Knorr cyclization. Using the optimized conditions, a variety of aliphatic and aromatic amines were subjected to acid-catalysed cyclization to give 2,5-di(selenophen-2-yl)pyrroles and 2,5-difuranylpyrroles (Scheme 2).

In general, aliphatic amines furnished the desired di(selenophen-2-yl)pyrroles and difuranyl pyrroles in good yields when compared to aromatic and heterocyclic amines. It is worthy to note that when long chain aliphatic amines, such as *n*-hexylamine, *n*-dodecylamine and *n*-hexadecylamine were employed, di(selenophen-2-yl)pyrroles were obtained in better yields than difuranylpyrroles (**2a**–**c** and **3a**–**c**, Scheme 2). However, there was no impact from the aliphatic chain length on the yield of either the furan- or selenophene-containing pyrroles. Substituted benzyl amines gave moderate yields in the case of di(selenophen-2-yl)pyrroles whereas difuranylpyrroles were obtained in lower yields (**2d**–**f** and **3d**–**f**). The reactions of different substituted anilines possessing neutral (phenyl), electron-donating (4-methoxy) and electron-withdrawing (4-fluoro) produced the heterocyclic products **2h**–**j** and **3h**–**j** in low yields compared to other amines. The 2,5-di(selenophen-2-yl)pyrroles and 2,5-difuranylpyrroles synthesized were fully characterized by ^{1}H, ^{13}C NMR, HR-MS and physical data (see Supplementary data).

The physical properties were recorded for all the di(selenophen-2-yl)pyrroles and difuranylpyrroles and the spectroscopic parameters for compounds **2a**–**d**, **3a**–**d**, **2f**–**g**, **3f**–**g**, **2i** and **3i** are listed in Table 1. Figure 2 shows the UV–vis spectra of **2a**, **3a** and **2i**. A bathochromic shift of the absorption maximum is observed for all 2,5-di(selenophen-2-yl)pyrroles, compared to the corresponding 2,5-difuranylpyrroles, which can be explained by the more aromatic nature of the di(selenophen-2-yl)pyrrole systems over the furanyl analogues. A significant bathochromic shift of the absorption maximum was observed for the monomers **2i**/**3i** and **2j**/**3j** over **2a**–**c**/**3a**–**c**, which can be explained by the extended conjugation due

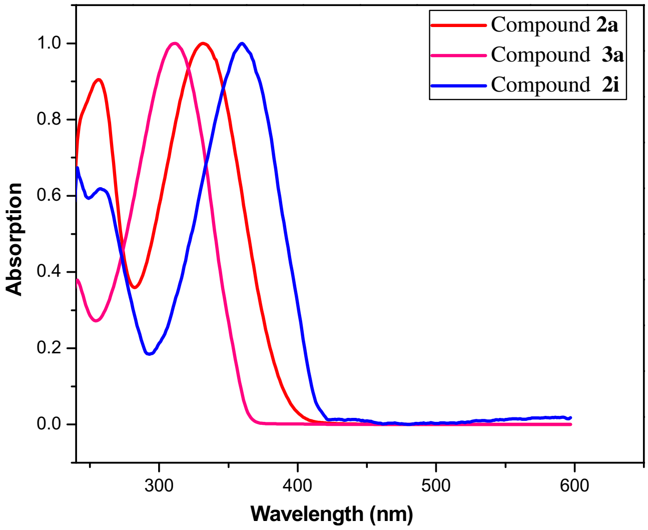


Figure 2. Absorption spectra of **2a**, **3a** and **2i** in dichloromethane.

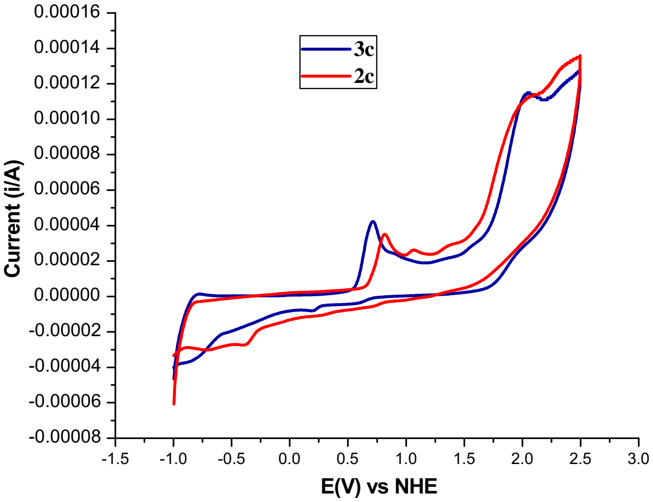


Figure 3. Cyclic voltammograms of **3c** and **2c** in dichloromethane at a scan rate of 50 mV/s.

Table 1
Spectroscopic features for selected compounds (**2a**–**d**, **3a**–**d**, **2f**–**g**, **3f**–**g**, **2i** and **3i**) in dichloromethane (c 2.5 × 10^{-5} mol/L)

Compound[a]	λ_{max}[b] (nm)	λ_{lum}[c] (nm)	E_g[d] (eV)	$^{1}E_{pa}$[e] (V)	E_{ox}^{onset} (eV)	HOMO[f]	LUMO[g]
2a	333	419	3.03	0.98	0.66	5.10	2.07
3a	313	385	3.36	0.92	0.55	4.99	1.63
2b	332	417	3.04	0.82	0.65	5.09	2.05
3b	312	370	3.32	0.72	0.53	4.97	1.65
2c	331	418	3.05	0.81	0.63	5.07	2.01
3c	313	379	3.26	0.69	0.54	4.98	1.72
2d	339	429	3.05	0.81	0.62	5.06	2.01
3d	316	391	3.36	0.77	0.56	5.00	1.64
2f	336	431	2.98	0.84	0.64	5.08	2.10
3f	315	385	3.37	0.76	0.51	4.95	1.58
2g	334	435	3.02	0.82	0.70	5.14	2.12
3g	314	354	3.36	0.78	0.63	5.07	1.71
2i	360	439	2.95	0.78	0.53	4.97	2.02
3i	335	392	3.36	0.72	0.56	5.00	1.64

[a] Spectroscopic properties for selected compounds.
[b] Measured in dilute dichloromethane solution.
[c] Excited at the absorption maxima.
[d] Estimated from the onset of absorption ($E_g = 1240/\lambda_{onset}$).
[e] ^{1}Epa denotes the first anodic peak potential.
[f] Calculated using the empirical equation: HOMO = $(4.44 + E_{ox}^{onset})$.
[g] Calculated from LUMO = HOMO − E_g.

to the substituted phenyl moiety. In addition, a bathochromic shift of the emission maximum was observed for all di(selenophen-2-yl)pyrroles over furanylpyrroles.

The electrochemical parameters of selected 2,5-di(selenophen-2-yl)pyrroles and 2,5-difuranylpyrroles are listed in Table 1. The experimental results show that the oxidation potentials of the difuranylpyrroles and di(selenophen-2-yl)pyrroles are less compared to dithienylpyrroles. The oxidation potentials of monomers **3c** and **2c** occur at +0.67 and +0.81, respectively, on a platinum disc electrode (Fig. 3). For the 2,5-di(selenophen-2-yl)pyrroles and 2,5-difuranylpyrroles, electrochemical polymer growth can be obtained by repeated cycling and the film is deposited on the working electrode after multiple cycles (see Supplementary data). From the experiment, it is obvious that the oxidation potentials of 2,5-difuranylpyrroles are less compared to 2,5-di(selenophen-2-yl)pyrroles. Similarly, the oxidation potentials of the monomers of the 2,5-di(selenophen-2-yl)pyrroles are lower than the terselenophene and the corresponding thienyl analogues.[17]

In summary, we have presented a two-step synthesis of an array of novel π-conjugated 2,5-di(selenophen-2-yl)pyrroles **2**, (SeNSe) and 2,5-difuranylpyrroles **3**, (ONO) via the Paal–Knorr reaction as a key step. Photophysical and electrochemical studies of the various products have been described. A bathochromic shift of the emission maximum is observed for all SeNSes over ONOs. The extended conjugation due to the presence of a phenyl moiety further promotes the bathochromic shift. These SeNSe and ONO derivatives exhibit lower oxidation potentials than those of their terselenophene and terthiophene analogues. Electropolymerization of the synthesized monomers is in progress in our laboratory.

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Supplementary data

Supplementary data (experimental procedures, compound characterization data and spectra) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.12.019.

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