Synthesis of Pyrroles annulated with Polycyclic Aromatic Compounds; Precursor Molecules for Low Band Gap Polymers

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Pyrroles annulated with polycyclic aromatic compounds, which are expected to be good precursor molecules for low band gap polymers, are prepared by the reaction of aromatic nitro compounds with ethyl isocyanoacetate and the subsequent deethoxycarbonylation.
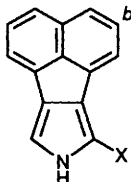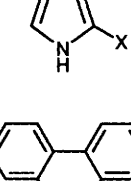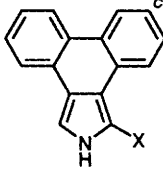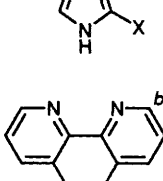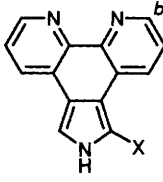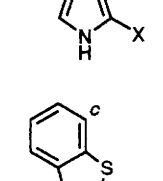
The band gap energy is a significant parameter for solid-state properties controlling intrinsic electronic and optical properties. One of the major challenges remaining in the field of organic conducting polymers is the design of narrow band gap materials in the undoped state. Calculations showed that the band gap is a function of the quinoid character of poly(pyrroles) or poly(thiophenes).[1] Therefore, pyrroles annulated with various kinds of polycyclic aromatic compounds are expected to be good precursors for poly(pyrroles) with a lowered band gap. Scheme 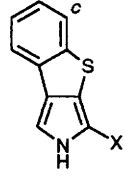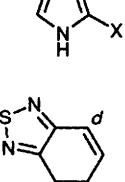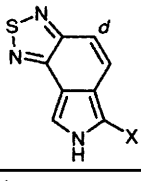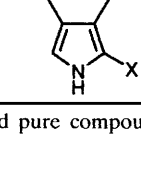1 shows our new strategy for the synthesis of such pyrroles or poly(pyrroles). Aromatic nitro compounds 1 may undergo the nucleophilic addition of ethyl isocyanoacetate to afford the annulated pyrrole 2, which is based on the reaction of aliphatic nitroalkenes with ethyl isocyanoacetate.[2] According to this Scheme, the original aromatic character of 1 can be recovered at the final quinoid structure of 5. Namely, the intrinsic electronic and optical character of the final poly(pyrroles) depends on the original aromatic character of 1.
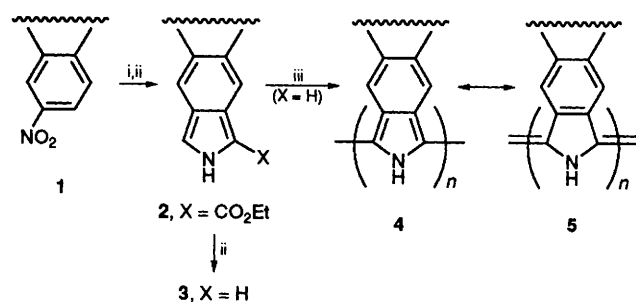
We have carried out the reaction of various aromatic nitro compounds with ethyl isocyanoacetate in the presence of DBU. As shown in Table 1, various aromatic nitro compounds gave the annulated pyrroles 2. Simple nitro aromatics such as nitrobenzene or 1-nitronaphthalene were not reactive so that the reaction proceeded very slowly to give the corresponding pyrroles in very low yields (the unconverted nitro aromatics were recovered in 80–90% yield). Although there has been a variety of nucleophilic aromatic substitution of hydrogen,[3] the present reaction is novel in that the driving force of the reaction is the recovery of the resonance energy *via* the annulation. The scope and limitations of this reaction are now under investigation. The ester function of 2 could be readily removed by heating with KOH in ethylene glycol at 170 °C to afford 3 which will be precursors for conducting poly(pyrroles) 4. Although some nitro compounds are not so reactive, the present method is very attractive for the preparation of isoindole derivatives such as 2 and 3. The existing methods for them require multistep procedures and lack in generality.[4] As aromatic nitro compounds are readily prepared by nitration of aromatic compounds, the present method provides a general and the simplest route for the synthesis of the annulated pyrroles such as 3.

The electrochemical behaviour of 3 was studied. The successive cyclic voltammograms of 3 by repeated potential scans at a Pt electrode in 0.1 mol dm^{-3} Bu$_4$NBF$_4$ between -0.6 and $+0.8$ V *vs.* SCE were measured. Growth of a polypyrrole film from 3a was observed as shown in Fig. 1. Similar growth was observed in the cases of 3d and 3e and conducting polypyrroles were formed from these pyrroles. Anodic oxidation of 3b gave the conductive material with σ *ca.* 10^{-2} S cm^{-1}, whose oxidation potential is 0.65 V *vs.* SCE. Elementary analysis shows that this material is (3b)$^+{}_2$A$^-$ (A = ClO$_4$ or BF$_4$). Although the exact structure of this material is not clear at the present stage, this may not be poly(pyrrole), for the oxidation potential of 3b is not shifted to the lower potential during anodic oxidation. The steric hindrance of this compound may inhibit the formation of poly(pyrroles). Anodic oxidation of 3a and 3e at a potential of 2 V gave the poly(pyrrole) film whose conductivity was about 1–4 S cm^{-1}.

Table 1 Preparation of pyrroles 2 and 3† at room temperature

Product		Yield (%)[a]
b	2a	70
	3a	72
c	2b	40 (75)[c]
	3b	65
b	2c	87
	3c	80
c	2d	60
	3d	60
d	2e	33
	3e	24

[a] Isolated pure compounds. [b] 4 h. [c] 10 h. [d] 48 h. [e] Based on consumed 1

Scheme 1 *Reagents and conditions*: i, CNCH$_2$CO$_2$Et, DBU, THF, room temp.; ii, KOH, HOCH$_2$CH$_2$OH, 170 °C; iii, Anodic oxidation, Bu$^n_4$NPF$_6$, MeCN

Table 2 Oxidation potential, conductivity, g values for the polymers from anodic oxidation of **3a** and **3g**

Pyrrole	Electrolyte[a]	Oxidation potential of polymers/V vs. SCE	Conductivity/S cm^{-1}[b]	g value[c]	Dopant/pyrrole[d]
3a	Bu$_4$NClO$_4$	0.04	1.4	2.0024	0.33
3a	Bu$_4$NPF$_6$		4.1	2.0026	0.20
3e	Bu$_4$NClO$_4$	0.14	2.1	2.0045	0.30
3e	Bu$_4$NBF$_4$		2.1	2.0034	0.28

[a] Pt, 2.0 V, MeCN. [b] Measured by four-probe DC method. [c] Measured against Li-TCNQ. [d] Calculated from elementary analysis.
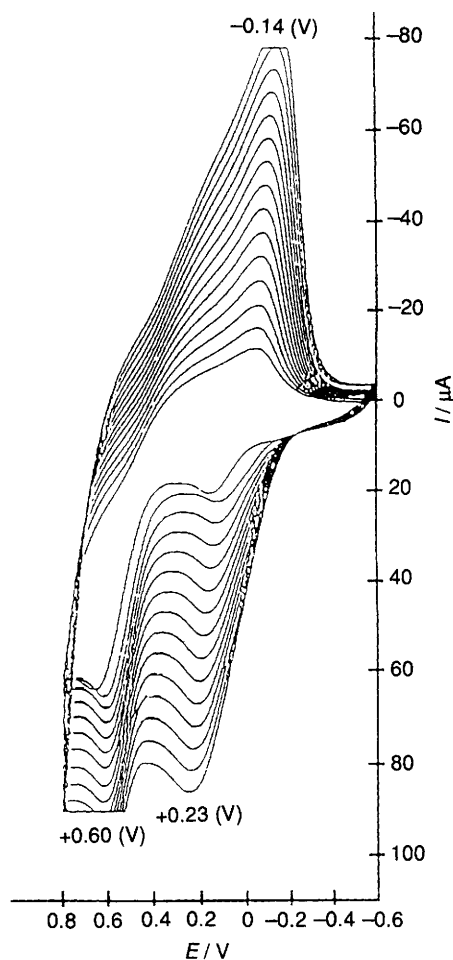

Fig. 1 Cyclic voltammogram of **3a** in CH$_2$Cl$_2$ solution Bu$_4$NClO$_4$ 0.1 mol dm^{-2} cast on a platinum electrode (potential relative to SCE). Sweep rate: 50 mVs^{-1}

These values are much higher than those of the poly(pyrroles) having substituents at the 3- and 4-positions.[5] In general, the introduction of substituents into N, 3 and 4 positions of pyrroles brings about a dramatic drop in the conductivity of the polymer, which makes the functionalization of poly-(pyrroles) with high conductivity very difficult.[6] Now, this difficulty is simply solved by the conversion of functionalized aromatic nitro compounds into pyrroles as shown here. The polymers derived from **3a** and **3e** have some interesting properties. Namely, the cation radicals formed by electro-chemical oxidation should be highly stabilized by the aromatic rings. Furthermore, functional group in the aromatic ring may provide an interesting feature. For example, the thiadiazole ring may induce the close intermolecular contact of S···N in the radical cation states.[7] The polymers derived from **3a** and **3e** shows ESR signals, g 2.0020–2.0045 (Table 2). The g value of the polymer derived from **3e** is significantly higher than that of the polymer of **3a**, which suggests that spins of polymer of **3e** are localized to the thiadiazole ring. These paramagnetic materials were very stable to air or water, the conductivity and

ESR signals of them were not affected after storage at room temperature for one year in a laboratory atmosphere. Annulated aromatics stabilize the positive charges in the doped polymers, which makes even more stable polymers than the conventional poly(pyrroles).

The UV–VIS–NIR spectrum of doped and undoped **3a** showed the absorption at about at 1350 and 600 nm, respectively, which suggested that the band gap of undoped polypyrrole **3a** was estimated to be about 2 eV. This value is considerably lower than that of unsubstituted poly(pyrrole) (3.2 eV).[5] Thus, we have presented a general route for the synthesis of pyrroles annulated with arenes **3** in a large structural variety, which will be used as precursors for con-ducting polymers. Further detailed investigations of electro-chemical and chemical polymerization of these molecules shown here and applications to electronic and optical mater-ials are in progress.

Footnote

† All compounds gave satisfactory elemental analysis. Spectroscopic data for pyrroles **2** and **3** are as follows: **2a**: mp 182–184 °C; ^{1}H NMR (CDCl$_3$) δ 1.51–1.58 (t, 3H), 4.47–4.55 (q, 2H), 7.18–7.19 (d, 1H), 7.49–7.78 (m, 4H), 8.09–8.11 (d, 2H), 9.03 (br, 1H); MS m/z 263 (M$^+$). **3a**: mp 129–131 °C; ^{1}H NMR (CDCl$_3$) δ 7.01 (d, 2H), 7.44–7.62 (m, 6H), 8.12 (br, 1H); MS m/z 191 (M$^+$); UV–VIS (nm) 356, 264, 246, 227.

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