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A Simple Way to Sequentially Connected Polycycles Containing Terminal Pyrrole Rings: Synthesis of Possible Precursors of Materials for Nonlinear Optics

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Abstract: the readily available 1,3-dioxolane-2-propanal allows the transformation of aromatic and heteroaromatic mono and dilithioderivatives into polycycles containing one or two pyrrole rings. Organolithiums bearing electron acceptor groups can be also employed affording possible precursors of materials for nonlinear optics.

The development of computing and signal-processing equipment operating at optical frequencies requires a wide choice of nonlinear optical materials and organic compounds seem to be particularly attractive in this respect. It is generally accepted that organic molecules with a high value of the molecular hyperpolarizability (β) must contain an electron acceptor group and an electron donor group separated by an extended Π structure such a benzene [1a], stilbene [2,1b], diphenylacetylene or diphenylbutadiyne [3], thiophene or 2,2'-dithiophene [4] systems. The use of electron rich heterocycles as donor groups has been already reported and furan or thiophene derivatives with structures tailored to reach high values of β have been obtained by the Pd°-catalyzed coupling of 2-furyl (or 2-thienyl) magnesium bromide (or zinc chloride) with aryl halides bearing cyano, nitro, ester and N,N-dialkylamide groups [5].

The pyrrole ring has been scarcely considered in this respect [6], although the presence of an N-H or N-R bond is attractive at least for two reasons: 1) chirality can be easily introduced into a pyrrole derivative through a chiral substituent at the position 1. This could be very helpful, since a macroscopic frequency doubling effect requires, besides β-values different from zero, a noncentrosymmetric environment such as a suitable crystal packing (easily obtainable from chiral molecules) or a poled polymer film [1]. 2) the N-H bond can be used to link the molecule to a polymer chain through proper spacers.

The literature examination showed that pyrrole organometallics suitable for the above mentioned Pd°-catalyzed couplings, a key reaction to obtain oligoheterocycles [7], have been however reported very recently [8]. The ring formation through the old Paal-Knorr synthesis [9] seems therefore to be the way to prepare suitable pyrroles designed for a preliminary investigation. Indeed, a recent paper describes the synthesis of a variety of 2-arylpyrroles [10] where protected 4-oxobutanals to be used in the Paal-Knorr synthesis are prepared either through the alkylation with bromoacetaldehyde dimethylacetal of the deprotonated N,N-dimethylhydrazones of

methylarylketones or through the reaction of the Grignard reagent from 2-(2-bromoethyl)-1,3-dioxolane with appropriate acyl derivatives.

In this work another approach is used to synthesize pyrrole derivatives with a structure designed to reach high values of β and proper organolithiums are reacted with a four carbon atom synthon to obtain substrates for the Paal-Knorr synthesis. As a matter of fact, it is well known [11] that synthetically useful organolithiums can be prepared by metal-halogen exchange or metal-hydrogen exchange even in the presence, as in this case, of electron acceptor, nucleophile-sensitive groups through a sensible choice of solvent, reagents and temperature. Moreover, the required acyl derivatives (i.e. the corresponding carboxylic acids) or methyl ketones are in many cases unknown and for their synthesis the same organometallics have to be considered.

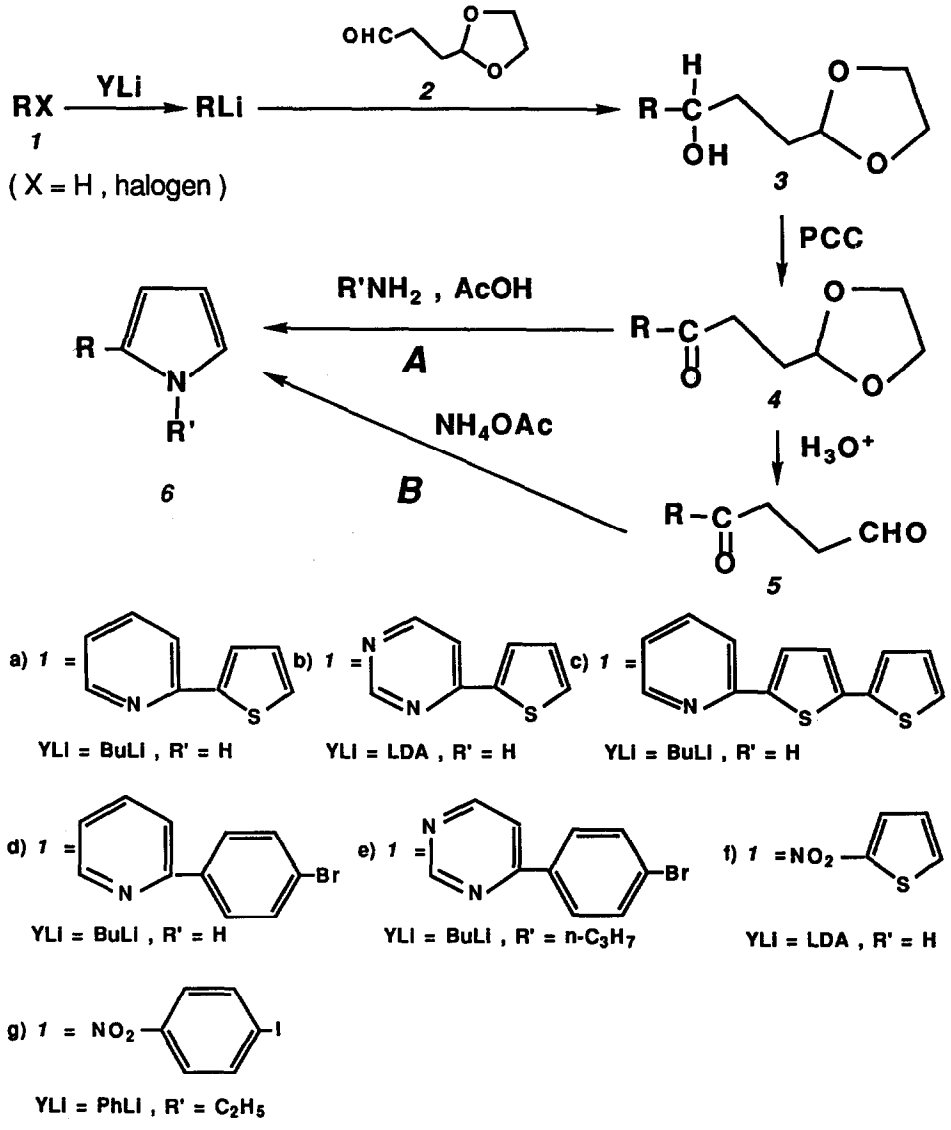
RESULTS

Pyrrole derivatives tailored to reach a high value of β have been prepared exploiting the electron poor pyridine and pyrimidine rings, besides the usual nitro group, as electron acceptors, separated from the electron donor pyrrole ring by benzene, thiophene or 2,2'-dithiophene systems. The aldehyde **2** revealed an attractive synthon, able to trap lithiated intermediates even at very low temperatures and allow the synthesis of pyrroles **6(a-g)** according to Scheme 1.

1,3-Dioxolane-2-propanal **2** previously obtained after a laborious synthesis [12] was readily prepared from commercially available 2-(2-bromoethyl)-1,3-dioxolane through the reaction of its Grignard reagent [13] with DMF. Carbinols **3** were oxidized to ketones **4** with pyridinium chlorochromate and were not characterized. Table 1 reports the overall yields in converting **1(a-g)** into **4(a-g)** together with the conditions used for their metalation.

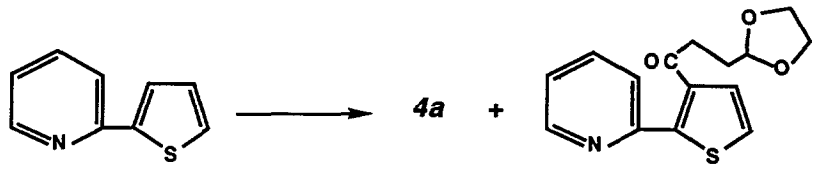
Table 1. Synthesis of Ketones **4**

1	Lithiation conditions	% Yield of **4**
2-(2-thienyl)pyridine (**1a**)	n-BuLi, THF, -20°C, 1h	49.6
4-(2-thienyl)pyrimidine (**1b**)	LDA, THF, -78°C, 15min	41.7
2-(5-(2-thienyl)-2-thienyl)pyridine (**1c**)	n-BuLi, THF, -15°C, 1h	40.0
2-(4-bromophenyl)pyridine (**1d**)	n-BuLi, THF, -78°C, 30min	56.0
4-(4-bromophenyl)pyrimidine (**1e**)	n-BuLi, THF:Ether=5:1, -95°C, 15min	9.8
2-nitrothiophene (**1f**)	LDA, THF, -78°C, 5min	45.6
4-nitroiodobenzene (**1g**)	PhLi, THF, -100°C, 15min	55.7



Scheme n. 1

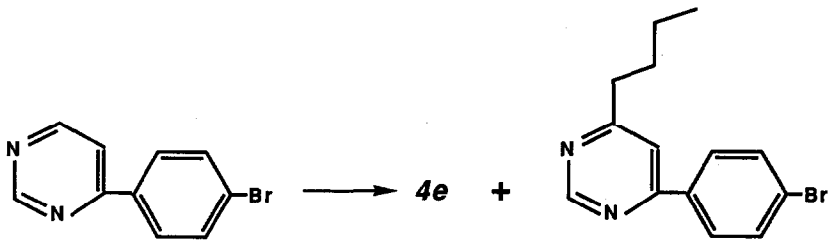
2-(2-thienyl)pyridine **1a** underwent lithiation mainly at the position 5 of the thiophene ring in agreement with the literature report [14] but a small amount of **7** (6.6%), isomer of **4a** deriving from reaction at the position 3 was isolated (Scheme 2).



1a *7*

Scheme n. 2

Since n-BuLi is reported to attack the pyrimidine ring of thienylpyrimidines [15], LDA was used to lithiate 4-(2-thienyl)pyrimidine **1b** at the position 5 of the thiophene ring in a synthetically useful yield. 5-bromopyrimidine [16a] and 4-(5-bromo-2-thienyl)pyrimidine [16b] are reported to undergo bromine / lithium exchange in good yields at -100°C and -78°C respectively: in spite of this, when the synthesis of **4e** was tried from 4-(4-bromophenyl)pyrimidine **1e**, easily prepared through a general synthetic scheme [17] from pyrimidine and 4-bromophenyllithium [18], the yield of **4e** was quite poor and some 4-(4-bromophenyl)-6-n-butylpyrimidine **8** (15.5%), deriving from the attack of the organolithium on the pyrimidine ring, was isolated (Scheme 3).



1e *8*

Scheme n. 3

No attempt to lithiate nitrothiophenes could be found in the literature except a short communication [19] on the lithiation of 3-nitrothiophene with no yields given: when **1f** was treated with LDA at -78°C a very dark colour developed but did not fade either after the addition of **2** or after the oxidation. Nevertheless, flash chromatography allowed the recovery of **4f** in satisfactory yield, together with some unreacted **1f**. Since nitrothiophenes are reported to be sensitive to amines [20], a slightly acidic hydrolysis was performed. 4-nitrophenyllithium was prepared from 4-nitroiodobenzene **1g** according to the literature prescription [21] and was converted to **4g** in satisfactory yield. It must be mentioned that 4-(4-nitrophenyl)-4-oxobutanal, a precursor of 2-(4-nitrophenyl)pyrroles closely related to **4g**, has been obtained through a long synthesis, including the ozone cleavage of a double bond [22].

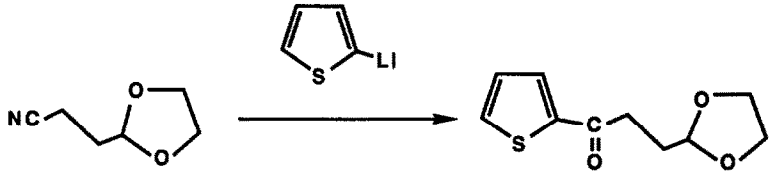
Table 2 reports ^{1}H and ^{13}C-NMR data of ketones **4(a-g)**.

Table 2. ^{1}H and ^{13}C-NMR data of Ketones **4** in $CDCl_3$

Compound	^{1}H-NMR (δ)	^{13}C-NMR (δ)
4a	8.59 (m, 1H), 7.71 (m, 3H), 7.57 (d, J= 4.0 Hz, 1H), 7.23 (m, 1H), 4.99 (t, J= 4.3 Hz, 1H), 3.90 (m, 4H), 3.05 (t, J= 7.4 Hz, 2H), 2.14 (m, 2H)	192.3, 151.8, 151.5, 149.9 144.4, 136.9, 132.5, 125.0 123.2, 119.6, 103.3, 65.0, 33.1, 28.3
4b	9.19 (d, J=1.4 Hz, 1H), 8.77 (d, J= 5.4 Hz, 1H) 7.77 (tight AB system, J= 4.0 Hz, 2H), 7.63 (dd, J= 5.4, 1.4 Hz, 1H), 5.01 (t, J= 4.2 Hz, 1H), 3.92 (m, 4H), 3.08 (t, J= 7.3 Hz,2H), 2.17 (m, 2H)	192.3, 159.3, 158.1, 157.8 148.3, 146.7, 132.2, 127.8, 115.9, 103.2, 65.1, 33.3, 28.2
4c	8.57 (m, 1H), 7.70 (m, 2H), 7.50 (d, J= 3.9 Hz, 1H), 7.32 (d, J= 3.9 Hz, 1H), 7.21 (m, 3H), 5.00 (t, J= 4.3 Hz, 1H), 3.92 (m, 4H), 3.02 (t, J= 7.4 Hz, 2H), 2.16 (m, 2H)	192.0, 151.8, 149.7, 145.6, 145.3, 142.3, 138.0, 136.7, 132.8, 126.4, 125.2, 124.4, 122.4, 118.7, 103.3, 65.0, 32.8, 28.3
4d	8.73 (m, 1H), 8.09 (s, 4H), 7.81 (m, 2H), 7.29 (m, 1H), 5.03 (t, J= 4.3 Hz, 1H), 3.92 (m, 4H) 3.17 (t, J= 7.4 Hz, 2H), 2.18 (m, 2H)	200.0, 156.2, 155.5, 149.9, 143.5, 137.1, 136.8, 128.5, 127.0, 122.8, 120.9, 103.5, 65.0, 32.6, 28.1
4e	9.33 (d,J= 1.4 Hz, 1H), 8.84 (d, J= 5.4 Hz, 1H) 8.16 (m, 4H), 7.79 (dd, J= 5.4, 1.4 Hz, 1H), 5.03 (t, J= 4.3 Hz, 1H), 3.94 (m, 4H), 3.18 (t, J= 7.3 Hz, 2H), 2.25 (m, 2H)	198.9, 162.7, 159.3, 157.8, 140.5, 138.7, 128.7, 127.4, 117.5, 103.4, 65.0, 32.7, 27.9
4f	7.90 (d, J= 4.3 Hz, 1H), 7.63 (d,J=4.3 Hz, 1H), 4.99 (t, J= 4.0 Hz, 1H), 3.91 (m, 4H), 3.06 (t, J= 7.2 Hz, 2H), 2.17 (m, 2H)	192.3, 156.2, 148.1, 129.6, 128.4, 102.8, 65.1, 32.9, 27.8
4g	8.22 (m, 4H), 5.01 (t, J= 4.1 Hz, 1H), 3.92 (m, 4H) 3.17 (t, J= 7.3 Hz, 2H), 2.03 (m, 2H)	197.9, 150.4, 141.5, 129.1, 123.8, 103.1, 65.1, 32.9, 27.9

Use of 1,3-dioxolane-2-propanenitrile **9** [23] was also considered as a more direct route to compounds **4** : a model reaction of this possible synthon with the easily prepared 2-thienyllithium was therefore tried (Scheme 4). The reaction, performed in ether at room temperature, afforded a moderate (35.1%) yield of 3-(1,3-dioxolan-2-yl)-1-(2-thienyl)-1-propanone **10** and about the same amount of **9** (29.3%). The change to thiophene Grignard reagents gave even worse results. Since many of the necessary lithium derivatives have to

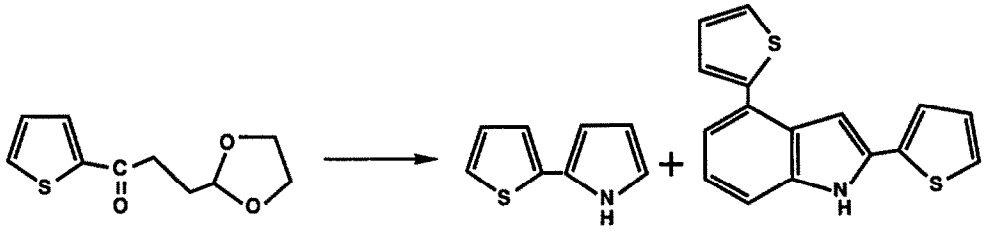
be prepared and used at low temperature, the low reactivity of **9** was found discouraging and the compound no longer used.



9 *10*

Scheme n. 4

Compounds **4d, 4e, 4g** were cleanly cyclized to pyrroles **6d, 6e, 6g** by ammonium acetate or primary amines in refluxing acetic acid in 67.8%, 69.4% and 86.1% yield respectively. When the reaction was tried on **4a** a complex mixture was formed from which **6a** was isolated in only 29.5% yield. To rationalize this disappointing result the same reaction was performed using the simpler thiophenic substrate **10**: a moderate yield (30.0%) of 2-(2-thienyl)-1H-pyrrole **11** [24] and a good yield (61.5%) of indole **12** were obtained (Scheme 5)



10 *11* *12*

Scheme n. 5

Since it is known that indoles are obtained from 1,4-dicarbonyl compounds and pyrroles in acidic conditions [25], it is reasonable to think that **12** could form from **11** and an excess of **10** : the electrophilic attack of a species originated from the cleavage of the acetal group on the pyrrole ring is a possible first step for this reaction, which is facilitated by the presence of the electron donor thiophene ring. Compound **12** is an oil that could not be crystallized and its structure was inferred from ^{1}H and ^{13}C-NMR and from MS data. In particular, the COSY spectrum of **12** reveals for a proton on the benzene ring two small (about 1 Hz) long range coupling constants: homonuclear decoupling experiments confirm this result and show no couplings for the broad, low-field signal of the proton in position 1 . Two very diagnostic long range coupling constants are reported for indoles, the 1-4 and the 3-7 one [26]: the above results agree with the presence of a 3-7 long range coupling and therefore with the structure **12**, rather then with the isomeric 2,7-bis(2-thienyl)-1H-indole. To avoid such relevant side reactions, the conversion of **4a, b, c, f** into the corresponding pyrroles was performed through the ketoaldehydes **5**, obtained from acidic hydrolysis of the corresponding precursors **4**

and cyclized using a mild procedure with ammonium acetate in ethanol [22], without any isolation (path B in Scheme 1). No by-products were formed and the pyrroles could be readily purified from the reaction tar using flash chromatography, but the yields remained moderate.

Table 3 shows ^{1}H and ^{13}C-NMR data for pyrroles **6(a-g)**.

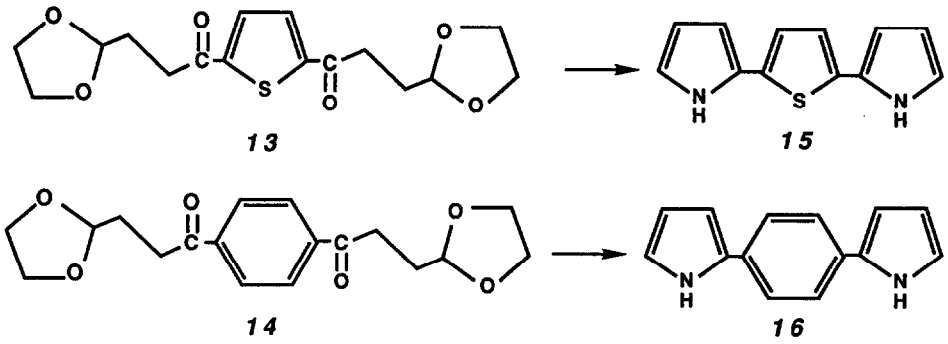
Table 3. ^{1}H and ^{13}C-NMR data of pyrroles **6(a-g)**

Compound	^{1}H-NMR (δ)	^{13}C-NMR (δ)
6a	8.55 (m, 1H), 8.45 (broad, 1H), 7.65 (m, 2H), 7.47 (d, J= 3.8 Hz, 1H), 7.13 (m, 1H), 7.03 (d, J= 3.8 Hz, 1H), 6.85 (m, 1H), 6.52 (m, 1H), 6.29 (m, 1H) (a)	152.6, 149.6, 141.5, 138.2, 136.5, 126.8, 125.2, 121.6, 121.5, 119.1, 118.4, 110.4, 107.3 (a)
6b	10.76 (broad, 1H), 9.02 (d, J= 1.4 Hz, 1H), 8.68 (dd, J= 5.5, 0.3 Hz, 1H), 7.90 (d, J= 4.0 Hz, 1H) 7.82 (dd, J= 5.5, 1.4 Hz, 1H), 7.30 (d, J= 4.0 Hz, 1H), 6.93 (m, 1H), 6.56 (m, 1H), 6.22 (m, 1H) (b)	159.7, 159.5, 157.9, 142.7, 138.6, 130.1, 126.9, 122.3, 121.1, 115.5, 110.6, 108.7 (b)
6c	10.64 (broad, 1H), 8.53 (m, 1H), 7.83 (m, 2H), 7.68 (d, J= 3.9 Hz, 1H), 7.24 (m, 3H), 7.19 (d, J= 3.8 Hz, 1H), 6.88 (m, 1H), 6.42 (m, 1H), 6.18 (m, 1H) (b)	153.0, 150.3, 144.2, 140.1, 137.6, 137.3, 134.2,126.7, 126.4, 125.6, 124.8, 122.9, 122.0, 120.3, 119.1, 110.3, 107.7 (b)
6d	8.82 (broad, 1H), 8.70 (m,1H), 8.00 (m, 2H), 7.74 (m, 2H), 7.57 (m, 2H), 7.23 (m, 1H), 6.87 (m, 1H), 6.63 (m, 1H), 6.34 (m, 1H) (a)	157.1, 149.7, 137.0, 136.7, 133.4, 131.7, 127.4, 124.0, 121.9, 120.2, 119.3, 110.3, 106.7 (a)
6e	9.28 (d, J= 1.3 Hz, 1H), 8.78 (d, J= 5.4 Hz, 1H) 8.13 (m, 2H), 7.75 (dd, J= 5.4, 1.3 Hz, 1H), 7.55 (m, 2H), 6.83 (m,1H), 6.27 (m, 2H), 3.96 (t, J= 7.4 Hz, 2H), 1.71 (m, 2H), 0.83 (t, J= 7.4 Hz, 3H) (a)	163.5, 159.1, 157.4, 136.6, 134.5, 133.3, 129.0, 127.2, 123.3, 116.8, 109.8, 108.1, 49.2, 24.8, 11.2 (a)
6f	10.99 (broad, 1H), 7.92 (d, J= 4.4 Hz, 1H), 7.22 (d, J= 4.4 Hz, 1H), 7.05 (m, 1H), 6.73 (m, 1H) 6.26 (m, 1H) (b)	147.6, 145.9, 131.6, 125.5, 123.5, 120.2, 111.5, 111.3 (b)
6g	8.25 (m, 2H), 7.52 (m, 2H), 6.89 (m, 1H), 6.35 (m, 1H), 6.27 (m, 1H), 4.05 (q, J= 7.3 Hz, 2H), 1.37 (t, J= 7.3 Hz, 3H) (a)	146.2, 140.1, 131.8, 128.3, 124.1, 123.9, 111.5, 109.1, 42.4, 16.7 (a)

(a) in $CDCl_3$; (b) in Acetone-*d6*

Three rings systems bearing two terminal pyrroles have become recently available and have been considered as precursors for electroactive polymers [27]. However, the reported four steps-synthesis, which transforms an intermediate already containing two pyrrole rings into a three ring system, fails if the central ring

has to be, for example, benzene.Therefore, to test the potential of the synthetic route in Scheme 1, the possibility of the simultaneous formation of two pyrrole rings from aromatic or heteroaromatic dilithioderivatives was investigated. 2,5-dilithiothiophene [28] and 1,4-dilithiobenzene (prepared from 1,4-dibromobenzene and t-butyllithium) were easily converted into **13** and **14** and their conversion into 2,2'-(2,5-thiophenediyl)bis-1H-pyrrole **15** [27] and 2,2'-(1,4-phenylene)bis-1H-pyrrole **16** was tried (Scheme 6). Appreciable yields of **15** (20.5%) and of **16** (44.9%) were obtained only when the cyclization was performed through path B of Scheme 1, using ammonium acetate and aqueous ammonia to avoid even the slightest acidity in the reaction mixture. Paal-Knorr syntheses in basic medium have been sometimes reported[29] and perhaps are worth of more consideration.



Scheme n. 6

It has been recently suggested that simple solvatochromism measurements could be used to select organic compounds with high values of β and even to obtain a measure of β itself [30]: this approach uses a two level model, which considers only the fundamental and the first excited electronic state, whose energy is assumed to be much lower than that of higher ones, considers β_{xxx} as the dominant term in the tensor quantity β (x being the direction of the permanent dipole moment in the molecule) and needs an estimate of the radius of the solvent cavity occupied by the molecule. β estimates comparable with those from EFISH [1a] experiments are claimed for a series of nitrobenzenes and pyridines, but later work finds no correlation of β with parameters from solvatochromic measurements for a series of diphenylacetylenes [3] and similar results are obtained, in a more qualitative way, for a series of stilbenes [2]. UV/VIS absorption maxima are however important in the characterisation of materials potential for nonlinear optics, because molecules with negligible absorption at about 400 nm ("colourless") could be used with solid-state lasers and suffer less photodegradation [1b]. UV/VIS spectra for pyrroles **6(a-g)**, **11** and **15** were measured in DMSO, Toluene, Acetonitrile and Hexane. The obtained values are shown in Table 4.

Two results clearly merge from this: 1) the UV/VIS spectra of **6(a-g)** are dominated by a high intensity band ($\varepsilon > 10^4$) lying in the near ultraviolet or visible range; the frequent presence of shoulders indicates that this band is not due to a single electronic transition. 2) nitroderivatives **6f** and **6g** show a similar behaviour to previously investigated nitrobenzenes and pyridines [30], with large red shifts going from hexane to more polar solvents: compound **6f** shows from hexane to DMSO a shift of 3230 cm^{-1}, comparable with that reported for 3-acetamido-4-dimethylaminonitrobenzene (DAN), 5580 cm^{-1}. This strong solvatochromism and the large shift

of the long wavelength maximum of **6f** compared with those of **11** and of 2-nitrothiophene (reported UV spectrum (isooctane): λ_{max} 298 nm (3.85) [31]) suggest a good deal of charge-transfer character for this band, again confirming the thiophene ring as a good electron pathway [4] .Three and four ring compounds **6** show a much less evident and more irregular solvatochromism: compound **15** with two pyrrole rings seems to follow a similar trend. These results are of difficult interpretation, but the solvatochromic approach has given poor results also with promising high β-molecules [2,3].

Table 4. UV/VIS Spectral Data (λ_{max} (Log ε)) of Pyrrole Derivatives

Compound	Hexane	Toluene	Acetonitrile	DMSO
6a	375 (sh, 4.32)	366 (4.39)	362 (4.42)	373 (4.42)
	361 (4.43)		269 (sh, 3.87)	
	250 (3.90)		247 (4.10)	
6b	(a)	385 (4.44)	382 (4.44)	397 (4.43)
			256 (3.88)	
6c	(a)	402 (4.49)	395 (4.51)	410 (4.52)
		314 (3.76)	311 (3.79)	
			240 (4.11)	
6d	340 (sh, 4.3) (b)	333 (4.48)	327 (4.50)	338 (4.49)
	328 (4.5)		240 (3.98)	
	240 (3.9)			
6e	338 (4.33)	341 (4.28)	334 (4.30)	344 (4.30)
	273 (sh, 3.76)		272 (sh, 3.77)	
	265 (sh, 3.83)		243 (4.07)	
	245 (4.09)			
6f	419 (sh, 4.2) (b)	426 (4.26)	438 (4.29)	462 (4.33)
	402 (4.3)		266 (3.85)	
	258 (3.9)			
6g	383 (sh, 3.97)	375 (4.08)	376 (4.09)	390 (4.09)
	366 (4.15)		238 (4.02)	
	356 (sh, 4.13)			
	268 (sh, 3.44)			
	260 (sh, 3.68)			
	253 (sh, 3.86)			
	234 (4.07)			
11	319 (sh, 3.90)			
	300 (4.14)			
15	(a)	379 (sh, 4.06)	375 (sh, 4.18)	376 (sh, 4.31)
		352 (4.33)	352 (4.40)	364 (4.40)
			230 (sh, 4.05)	

(a) Insoluble; (b) Too insoluble for an accurate ε determination

Compounds **6(a-g)** have λ_{max} in the range of high β stilbene derivatives and some (**6d, 6e**) approach "colourless" nonlinear optical materials as well [1b]: besides, very little is known about the nonlinear optical properties of oligoheterocycles containing different rings [32]. Compounds **6** are on this ground worth a deeper investigation through EFISH measurements.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. ^{1}H-NMR spectra were measured at 300 or 200 MHz on Bruker AC-P 300 or AC-F 200 instruments on which ^{13}C-NMR spectra were acquired using composite pulse decoupling. A Cary 118 instrument was used to record the UV/VIS spectra, using freshly opened Spectrograde solvents. Mass spectra were obtained on a Varian CH-5 instrument at 70 eV. Flash chromatographic separations were performed using silica gel (230-400 Mesh, Merck) and 30 or 35 mm wide columns: a sample loading of about 1g / 100g silica gel was used and each eluent is reported at its appropriate point. Petrol refers to 40-60 °C petroleum ether. 4-(2-thienyl)pyrimidine **1b**[17], 2-(5-(2-thienyl)-2-thienyl)pyridine **1c** [33], 2-(4-bromophenyl)pyridine **1d** [34] were prepared following the literature. 4-nitrophenyllithium was quenched at -100 °C with **2** : work-up and oxydation followed the general procedure. Solutions were routinely dried with sodium sulfate.

1,3-Dioxolane-2-propanal (2)

To the Grignard reagent obtained from 2-(2-bromoethyl)-1,3-dioxolane (20.02g ; 0.111 mol) in THF (120 ml) dry DMF (9.5 ml ; 0.123 mol) was added with stirring for 10 minutes. The mixture was stirred for 90 min. at room temperature, then citric acid monohydrate (23.4 g ; 0.111 mol) in water (70 ml) was added. The organic layer was separated, the aqueous layer extracted with ether (20 ml) five times, the organic layers were combined and dried . The solvent was evaporated and the residue distilled under vacuum. Yield 57.1%, bp. 85-90 °C / 18 Torr, spectral data coincident with those reported.

Synthesis of carbinols 3

Method A (for **3b, 3f**) A solution of LDA was prepared at -78 °C in THF (24 ml) from diisopropylamine (0.98 ml ; 7.0 mmol) and n-butyllithium in hexane (4.1 ml ; 1.7 M). Compounds **1b** and **1f** (6.0 mmol) were added at -78 °C in THF (3ml), the mixture further stirred at -78 °C (for reaction times, see Table 1) and 1,3-dioxolane-2-propanal **2** (0.911 g ; 7.0 mmol) was added in THF (3 ml). Stirring was continued for 10 minutes at -78 °C, the cooling bath was removed and saturated ammonium chloride (10 ml) added (into the reaction mixture from **1f** concentrated hydrochloric acid (1.2 ml) was also added). The organic layer was separated, the aqueous layer extracted with ether (10 ml) five times, the combined organic layers were dried and the solvent removed by aspirator vacuum. The raw, oily carbinols **3b** and **3f** were directly oxidized without any purification.

Method B (for **3a, 3c, 3d**) Compounds **1a, 1c, 1d** (5 mmol) in THF (25 ml) were cooled to a suitable temperature and n-butyllithium in hexane (3.6 ml ; 1.7M) was added. The reaction mixture was further stirred

(for the reaction times and temperatures, see Table 1), then 1,3-dioxolane-2-propanal **2** (0.781 g ; 6.0 mmol) in THF (2 ml) was added. The mixture was further stirred for 1 hour at low temperature, then the cooling bath was removed and saturated ammonium chloride (5 ml) added. The organic layer was separated, the thin aqueous layer extracted with ether (20 ml), the organic layers were combined and dried ; removal of the solvent left residues of crude **3a, 3c, 3d** that were directly used for the oxidation.

Method C (for **3e***)* 4-(4-bromophenyl)pyrimidine (**1e**) was prepared accordingly to the procedure for 4-(2-thienyl)pyrimidine from pyrimidine and 4-bromophenyllithium in ether. Yield 53.5% . Mp. 86-87 °C (hexane). ^{1}H-NMR ($CDCl_3$) (δ) 9.27 (d, J= 1.3 Hz, 1H), 8.79 (dd, J= 5.4, 0.3 Hz, 1H), 7.98 (m, 2H), 7.66 (m, 3H). ^{13}C-NMR ($CDCl_3$) (δ) 162.7, 159.2, 157.7, 135.4, 132.3, 128.6, 125.9, 116.7. Calcd. for $C_{10}H_7N_2Br$: C, 51.09; H, 3.00; N, 11.92. Found: C, 51.24; H, 2.89; N, 12.12. **1e** (2.005 g ; 8.53 mmol) in a 5:1 THF/ether mixture (60 ml) was cooled to -95 °C (internal temperature) with a liquid nitrogen / ethanol bath. N-butyllithium (5.5 ml ; 1.7M). was slowly added for 10 min. with vigorous stirring, then the orange mixture was further stirred for 5 min. at -95 °C and quenched with 1,3-dioxolane-2-propanal **2** (1.347 g ; 10.35 mmol) in THF (4 ml). Stirring was continued for 10 min., the cooling bath removed and saturated ammonium chloride (5 ml) added. The organic layer was separated, the thin aqueous layer extracted with THF (20 ml), the combined organic layers dried and the solvent removed. Oxidation was then performed with the raw, oily product.

Synthesis of ketones 4

The crude carbinols **3** obtained from 5 mmol of substrate **1** in dry dichloromethane (5 ml) were added to the suspension of pyridinium chlorochromate (1.941 g ; 9.00 mmol) and sodium acetate (0.280 g ; 3.40 mmol) in dry dichloromethane (5 ml) (for carbinols **3b, 3f, 3e, 3g** all these amounts were correspondingly altered). The mixture was stirred for 90 min. at room temperature, pyridinium chlorochromate (0.194 g ; 0.90 mmol) was added and stirring continued for one hour. Saturated sodium hydrogen carbonate was added until no more carbon dioxide developed, the heterogeneous mixture was filtered and the solid residue washed on the filter with dichloromethane (60 ml). The organic phase from the filtrate was separated, dried and the solvent removed at reduced pressure. The residue was purified through a flash chromatography.

3-(1,3-Dioxolan-2-yl)-1-(5-(2-pyridyl)-2-thienyl)-1-propanone (**4a**). (Eluent: acetone / petrol=1/1). Mp. 123-4 °C.(Ethyl acetate/ether). Calcd. for $C_{15}H_{15}N0_3S$: C, 62.26; H, 5.22; N, 4.84. Found: C, 61.98; H, 5.21; N, 4.94. By-products: **1a** (9.9%), 3-(1,3-dioxolan-2-yl)-1-(2-(2-pyridyl)-3-thienyl)-1-propanone **7** (6.6%). Oil. ^{1}H-NMR ($CDCl_3$) (δ) 8.60 (m, 1H), 7.71 (m, 2H), 7.34 (tight AB-system, J= 5.3 Hz, 2H), 7.22 (m, 1H), 4.94 (t, J= 4.3 Hz, 1H), 3.84 (m, 4H), 2.90 (t, J= 7.2 Hz, 2H), 2.09 (m, 2H). ^{13}C-NMR ($CDCl_3$) (δ) 198.2, 151.9, 149.3, 146.8, 138.6, 136.4, 128.9, 126.2, 123.4, 122.8, 103.4, 64.9, 36.6, 28.2. EIMS, *m/z (%)* : 289 (M^+, 21).

3-(1,3-Dioxolan-2-yl)-1-(5-(4-pyrimidinyl)-2-thienyl)-1-propanone (**4b**). (Eluent: acetone / petrol=1/2). Mp. 148-9 °C (Ethyl acetate) Calcd. for $C_{14}H_{14}N_2O_3S$: C, 57.92; H, 4.86; N, 9.64. Found: C, 58.18; H, 4.79; N, 9.93. By-product: **1b** (4.7%)

3-(1,3-Dioxolan-2-yl)-1-(5-(5-(2-pyridyl)-2-thienyl)-2-thienyl)-1-propanone (**4c**). The crude product was crystallized from ethanol to give **4c**. Mp. 137-9 °C (Ethyl acetate). Calcd. for $C_{19}H_{17}NO_3S_2$: C, 61.43; H, 4.61; N, 3.77. Found: C, 61.58, H, 4.50; N, 3.96. The mother liquor was evaporated and the residue, a

very complex (TLC) mixture, was subjected to a flash chromatography (Eluent: acetone / petrol=1/10) to recover some **1c** (6.6%).

3-(1,3-Dioxolan-2-yl)-1-(4-(2-pyridyl)phenyl)-1-propanone (**4d**). (Eluent : acetone / petrol=1/5). Mp. 124-5 °C (Ethyl acetate). Calcd. for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.35; H, 6.08; N, 5.02.

3-(1,3-Dioxolan-2-yl)-1-(4-(4-pyrimidinyl)phenyl)-1-propanone (**4e**). (Eluent: acetone / petrol=1/4). Mp. 112-4 °C (Acetone/ether). Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.21; H, 5.55; N, 9.74. By-product: 4-(4-bromophenyl)-6-n-butylpyrimidine **8** (15.5%). Oil. ^{1}H-NMR ($CDCl_3$) (δ) 9.16 (d, J=1.3 Hz, 1H), 7.96 (m, 2H), 7.63 (m, 2H), 7.54 (d, J=1.3 Hz, 1H), 2.82 (t, J=7.8 Hz, 2H), 1.78 (m, 2H), 1.44 (m, 2H), 0.96 (t, J=7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$) (δ) 171.7, 162.5, 158.8, 135.8, 132.2, 128.6, 125.5, 115.6, 37.8, 31.0, 22.5, 13.9. EIMS, *m/z (%)*: 292 (M^+ + 2, 6), 290 (M^+, 6), 250 (98), 248 (M^+- C_3H_6, Mc Lafferty rearrangement, 100).

3-(1,3-Dioxolan-2-yl)-1-(5-nitro-2-thienyl)-1-propanone (**4f**). (Eluent: acetone/petrol=1/4). Mp. 88-9°C (Ethyl acetate/ether). Calcd. for $C_{10}H_{11}N0_5S$: C, 46.69; H, 4.31; N, 5.44. Found: C, 46.99; H, 4.29; N, 5.73. By-product: **1f** (16.8%)

3-(1,3-Dioxolan-2-yl)-1-(4-nitrophenyl)-1-propanone (**4g**). (Eluent: acetone/petrol=1/4). Mp. 108-10 °C (Ethyl acetate/ether). Calcd. for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.21; N, 5.57. Found: C, 57.67; H, 5.20; N, 5.86.

3-(1,3-Dioxolan-2-yl)-1-(2-thienyl)-1-propanone (10)

Thiophene (2.2 ml ; 27.5 mmol) in ether (30 ml) was added of n-butyllithium in hexane (16.2 ml ; 1.7M) and stirred for one hour. 1,3-Dioxolane-2-propanenitrile **9** (3.51 g; 27.6 mmol) in ether (15ml) was then added and stirring continued for 90 min. Saturated ammonium chloride (20 ml) and concentrated hydrochloric acid (2.5 ml) were added, the organic layer was separated, the aqueous layer extracted three times with ether (20 ml). The combined ethereal extracts were dried and the solvent evaporated: compound **9** was removed on a boiling water bath at 0.1 torr and collected at -78°C; 1.03 g (29.3%) were recovered. The residue was purified through a flash chromatography (Eluent: ethyl acetate / petrol=1/3) to give **10** (35.1%). Bp. 103 °C / 0.01 Torr. ^{1}H-NMR ($CDCl_3$) (δ) 7.75 (dd, J=3.8, 1.1 Hz, 1H), 7.64 (dd, J=5.0, 1.1 Hz, 1H), 7.13 (dd, J=5.0, 3.8 Hz, 1H), 4.99 (t, J=4.3 Hz, 1H), 3.92 (m, 4H), 3.05 (t, J=7.4 Hz, 2H), 2.14 (m, 2H). ^{13}C-NMR ($CDCl_3$) (δ) 192.3, 144.2, 133.4, 131.9, 128.1, 103.3, 65.0, 33.1, 28.1. Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70; S, 15.10. Found: C, 56.26; H, 5.55; S, 14.78.

Synthesis of pyrroles 6

Method A (Pyrroles **6d, 6e, 6g, 11**) Ketones **4** (2 mmol) in acetic acid (8 ml) were refluxed under nitrogen with the appropriate primary amine (24 mmol) or with ammonium acetate (1.85 g, 24 mmol. Acetic anhydride was also added (0.7 ml)) until no more **4** was present (TLC). The mixture was poured into water (50 ml), neutralized with solid sodium hydrogen carbonate and extracted three times with dichloromethane (20 ml). The combined organic layers were dried and after removal of the solvent purified by flash chromatography.

2-(4-(2-1H-Pyrryl)phenyl)pyridine (**6d**). (Eluent: acetone / petrol= 1/5) Yield 67.8%. Mp. 195-7 °C (Benzene). Calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.68; H, 5.36; N, 12.74. EIMS, *m/z (%)*: 220 (M^+, 100).

4-(4-(1-n-Propyl-2-1H-pyrryl)phenyl)pyrimidine (**6e**). (Eluent: acetone / petrol=1/4). Yield 69.4%. Mp. 68-70 °C (Ether/pentane). Calcd. for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.81; H, 6.51; N, 16.28. EIMS, *m/z (%)*: 263 (M^+, 100).

1-Ethyl-2-(4-nitrophenyl)-1H-pyrrole (**6g**). (Eluent: acetone / petrol=1/5). Yield 86.1%. Mp. 87-9 °C (acetone/hexane). Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.69; H, 5.58; N, 13.19. EIMS, *m/z (%)*: 216 (M^+, 100).

2-(2-Thienyl)-1H-pyrrole (**11**) and 2,4-bis(2-thienyl)-1H-indole (**12**). (Eluent: acetone / petrol=1/10). **11**: yield 30.0%. Mp.78-80 °C (subl. at 100 °C/ 0.3 torr, lit. 78 °C). **12** : oil. ^{1}H-NMR (acetone-*d6*) (δ) 10.95 (broad, 1H), 7.54 (m, 2H), 7.40 (m, 3H), 7.33 (dd, J= 7.3, 0.9 Hz, 1H), 7.18 (m, 3H), 7.09 (dd, J= 5.1, 3.6 Hz, 1H). ^{13}C-NMR ($CDCl_3$) (δ) 143.6, 137.3, 135.4, 133.0, 127.8, 127.6, 126.7, 126.5, 124.7, 124.6,124.5, 123.2, 122.5, 119.7, 110.3, 99.9. EIMS, *m/z (%)*: 281 (M^+, 80%).

Method B (Pyrroles **6a**, **6b**, **6c**, **6f**) Ketones **4** (1.2 mmol) in dioxane (6 ml) were added to 2N hydrochloric acid (6 ml), the mixture was degassed and stirred for 24 hours under nitrogen. Saturated sodium hydrogen carbonate was then added up to neutrality and the mixture extracted three times with dichloromethane (20 ml). The insoluble ketoaldehyde **5c** was simply filtered off, washed with water and dried under vacuum. The combined organic layers were dried, evaporated and the residue dissolved in ethanol (3 ml), added to solid ammonium acetate (0.95 g; 12.3 mmol). To obtain **6f** acetic acid (0.7 ml) was also added; to obtain **6c** ammonium acetate (5g) and ethanol (20 ml) were used.The mixture was refluxed under nitrogen 30 min. then poured into water (50 ml) and extracted three times with dichloromethane (20 ml). The combined organic layers were dried, evaporated and the residue purified through a flash chromatography.

2-(5-(2-1H-Pyrryl)-2-thienyl)pyridine (**6a**). (Eluent: acetone / petrol=1/4). Yield 34.6%. Mp. 122-4 °C (Toluene/cyclohexane) . Calcd. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38. Found: C, 68.69; H, 4.40; N, 12.33. EIMS, *m/z (%)*: 226 (M^+, 100).

4-(5-(2-1H-Pyrryl)-2-thienyl)pyrimidine (**6b**). (Eluent: acetone / petrol=1/2). Yield 44.5%. Mp. 167-9 °C (Chloroform). Calcd. for $C_{12}H_9N_3S$: C, 63.41; H, 3.99; N, 18.49. Found: C, 63.10; H, 3.87; N, 18.59. EIMS, *m/z (%)*: 227 (M^+, 100).

2-(5-(5-(2-1H-Pyrryl)-2-thienyl)-2-thienyl)pyridine (**6c**). (Eluent: acetone / petrol=1/3). Yield 36.4%. Mp. 200-3.5 °C (Acetone/hexane). Calcd. for $C_{17}H_{12}N_2S_2$: C, 66.20; H, 3.92; N, 9.08. Found: C, 65.90; H, 3.92; N, 9.12. EIMS, *m/z (%)*: 308 (M^+, 100).

2-(5-Nitro-2-thienyl)-1H-pyrrole (**6f**). Eluent: acetone / petrol=1/4).Yield 54.7%. Mp. 153-5 °C (Acetone/hexane). Calcd. for $C_8H_6N_2O_2S$: C, 49.47; H, 3.11; N, 14.42. Found: C, 49.45; H, 3.03; N, 14.33. EIMS, *m/z (%)*: 194 (M^+, 100).

*1,1'-(1,4-Phenylene)bis (3-(1,3-dioxolan-2-yl)-1-propanone) (**14**)*

1,4-dibromobenzene (0.755 g; 3.20 mmol) in ether (10 ml) at -50 °C was treated with t-butyllithium in pentane (10 ml; 1.4M) and stirred at -40 /-50 °C for 90 min. 1,3-Dioxolane-2-propanal **2** (1.004 g; 7.71 mmol) in THF (25 ml) was then added and the mixture stirred 30 min. The cooling bath was removed and stirring

continued 30 min. at room temperature. Saturated ammonium chloride (5 ml) was then added, the organic layer was separated, the thin aqueous phase extracted two times with ethyl acetate (10 ml): the combined organic layers were dried and the solvents removed by reduced pressure. The oily residue was dissolved in dichloromethane (12 ml) and added to the suspension of pyridinium chlorochromate (2.666 g; 12.37 mmol) and sodium acetate (0.300 g; 3.66 mmol) in dichloromethane (5 ml). The mixture was stirred for 70 min., added with ether (20 ml) and filtered through a short (about 2 cm) Florisil^R plug. The plug was further washed with dichloromethane/ether (1/1, 100 ml) and the combined organic percolates evaporated at reduced pressure. The residue was dissolved in acetone (5 ml) and ether (30 ml) was added: the white precipitate of **14** was filtered, washed with ether and dried: yield 39.8%. Mp. 123-4 °C (Ethyl acetate). ^{1}H-NMR ($CDCl_3$) (δ) 8.04 (s, 4H), 5.01 (t, J=4.2 Hz, 2H), 3.95 (m, 8H), 3.14 (t, J=7.2 Hz, 4H), 2.17 (m, 4H). ^{13}C-NMR ($CDCl_3$) (δ) 198.9, 140.0, 128.2, 103.3, 65.0, 32.8, 27.8. Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.76; H, 6.63.

1,1'-(2,5-Thiophenediyl)bis(3-(1,3-dioxolan-2-yl)-1-propanone) (13). Similarly obtained from 2,5-dibromothiophene (0.78 ml; 6.92 mmol) in THF (40 ml) through 2,5-dilithiothiophene. Yield 46.4%. Mp. 128-9 °C (Isopropanol). ^{1}H-NMR ($CDCl_3$) (δ) 7.77 (s, 2H), 5.00 (t, J=4.2 Hz, 2H), 3.96 (m, 8H), 3.06 (t, J=7.3 Hz, 4H), 2.18 (m, 4H). ^{13}C-NMR ($CDCl_3$) (δ) 192.6, 148.6, 131.4, 103.1, 65.1, 33.5, 28.1. Calcd. for $C_{16}H_{20}O_6S$: C, 56.47; H, 5.92. Found: C, 56.34; H, 5.86.

2,2'-(2,5-Thiophenediyl)bis-1H-pyrrole (15)

Compound **13** (0.407 g; 1.20 mmol) in dioxane (6 ml) was added to 2N hydrochloric acid (6 ml) and the hydrolysis step was performed as reported for **4a**, **4b**, **4f**: the hydrolysis time was brought to 48 hr. The raw product from the acetal cleavage was put into a 25-ml flask with a small stirring bar and aqueous 25% ammonium hydroxide (0.4 ml), ethanol (10 ml) and solid ammonium acetate (1.85 g; 24.0 mmol) were added. The flask was tightly stopped with a rubber bung and the mixture stirred for 20 min. at 90 °C. After cooling it was poured into water (50 ml) and the raw green organic product extracted four times with dichloromethane (15 ml). The solvent was removed from the combined and dried organic layers and the residue purified through a flash chromatography (Eluent: acetone/petrol=1/4).Yield 20.5%. Mp. 206-8 °C (Dec; after sublimation at 170 °C/ 0.01 torr. Literature reports 194-6 °C (dec)). Calcd. for $C_{12}H_{10}N_2S$: C, 67.26; H, 4.71; N, 13.07. Found: C, 67.20; H, 4.64; N, 13.26.

2,2'-(1,4-Phenylene)bis-1H-pyrrole (16). The cyclization of compound **14** to compound **16** took place following the above described procedure. When the cyclization mixture was poured into water a solid separated which was filtered, washed with water, dried under vacuum and purified by flash chromatography (Eluent: ethyl acetate/petrol=1/2). Yield 44.9%. Mp. decomposes between 298 and 307 °C (Acetonitrile). ^{1}H-NMR (acetone-d_6) (δ) 10.10 (broad, 2H), 7.63 (s, 4H), 6.85 (m, 2H), 6.52 (m, 2H), 6.17 (m, 2H). ^{13}C-NMR (acetone-d_6) (δ) 132.4, 131.6, 124.7, 119.7, 110.2, 106.1. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45; Found: C, 80.52; H, 5.73; N, 13.61. EIMS, *m/z (%)*: 208 (M^+, 100)

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