Push-Pull Tricyanovinyl-Substituted Thienylpyrroles: Synthesis, Solvatochromic and Electrochemical Properties

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Abstract. New tricyanovinyl- derivatives *1* of 1-(alkyl)aryl-2-(2´-thienyl)pyrroles *2* have been synthesized and characterized. Compounds *1* display dramatic reductions in both their optical and electrochemical band gaps in comparison to thienylpyrroles *2*. The solvatochomic behavior of tricyanovinyl- derivatives *1* was investigated in a variety of solvents. In agreement with the solvatochromic and the electrochemical studies for push-pull derivatives *1* the new compounds prepared, can find application for manufacturing new materials with notable non-linear optical properties.

Introduction

Novel conjugated organic molecules containing both donor and acceptor moieties have attracted much attention because they are critical components for many great advanced technologies such as non-linear optical (NLO), photo- and electroluminescent devices, and photovoltaic devices. Organic NLO materials have many advantages over inorganic materials, such as large nonlinear optical coefficients, greater ease for synthetic design, easy preparation and lower cost [1]. It has been revealed that the second order hyperpolarizabilities (β) of heterocyclic chromophores are often higher than their benzene analogues [2]. Recently we have also demonstrated that donor-acceptor substituted bithiophenes and terthiophenes have many favorable features as NLO materials [3-6]. Use of conjugated thiophene and pyrrole derivatives as donors combined with substituted acceptor groups are promising candidates among such D-A systems due to their numerous applications. Unlike the thiophene or furan analogues, the pyrrole ring can be further substituted on the nitrogen atom so that the electron density of the chromophore can be changed. In addition, replacing N-H group of the pyrrole ring with another substituent would eliminate some intramolecular hydrogen bonding which might also affect their macroscopic structures and NLO properties [7]. In the last few years the donor substituted tricyanovinyl compounds have received a lot of interest. Due to their electrical conductivity and strong solvatochromic properties, which mainly originate from their donor-acceptor substitution, they can be used as model compounds for dyes with strong NLO properties [7-8]. Therefore, trycianovinyl- derivatives *1* represent promising candidates for NLO and for others applications. As part of our continuing interest in non-linear optical material [3-6, 9-11], we have synthesized new tricyanovinyl-substituted thienylpyrroles *1*, by tricyanovinylation reaction of 1-alkyl(aryl)-2-(2´-thienyl)pyrroles *2* described by us recently [11].

Results and discussion

Our recent reported synthesis of thienylpyrroles *2* [11] made these compounds available in reasonable amounts, ready for further applications. The synthesis of tricyanovinyl-substituted thienylpyrroles *1* is outline in Scheme 1. This functionalization was introduced in a manner similar to previously reported procedure [3] by reacting pyrroles *2* with TCNE in DMF for 15min.-3h at rt. Tricyanovinylation of thienylpyrroles *2* was made selectively at the 5-position of pyrrole ring to give compounds *1* in fair to good yields (12-73%), (Scheme 1, Table 1). These results are in accordance with the greater nucleophilicity of the pyrrole ring *versus* the thiophene ring as it has been shown earlier in the case of formylation of thienyl-pyrroles [12].
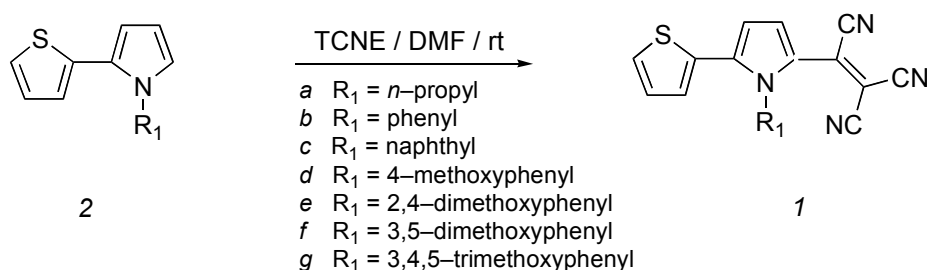

TCNE / DMF / rt

a R_1 = *n*–propyl
b R_1 = phenyl
c R_1 = naphthyl
d R_1 = 4–methoxyphenyl
e R_1 = 2,4–dimethoxyphenyl
f R_1 = 3,5–dimethoxyphenyl
g R_1 = 3,4,5–trimethoxyphenyl

Table 1- Yields, IR and UV-visible data of pyrroles *2* and tricyanovinyl-thienylpyrroles *1*.

Entry	Comp.	λ_{max}*[nm] (ε)	Comp.	R	Yield [%]	λ_{max}*[nm] (ε)	$h\upsilon_{>>>}$ [eV]	IRυ_{CN} [cm^{-1}]
1	*2a*	291.0 (1,800)	*1a*	*n*-propyl	12	491.5 (16,640)	2.52	2215
2	*2b*	294.5 (9,208)	*1b*	phenyl	35	511.5 (19,086)	2.42	2211
3	*2c*	288.5 (15,638)	*1c*	naphthyl	34	516.5 (32,160)	2.40	2207
4	*2d*	290.0 (11,410)	*1d*	4-methoxyphenyl	50	519.0 (31,639)	2.39	2212
5	*2e*	286.5 (10,093)	*1e*	2,4-dimethoxyphenyl	63	525.5 (36,407)	2.36	2210
6	*2f*	282.0 (9,950)	*1f*	3,5-dimethoxyphenyl	37	514.5 (24,604)	2.41	2216
7	*2g*	281.5 (8,477)	*1g*	3,4,5-trimethoxyhenyl	73	519.0 (30,842)	2.39	2207

*All the UV/vis spectra were run in ethanol.

UV-visible study. Electronic absorption spectra of all push-pull compounds *1a-g* show an intense lowest energy charge-transfer absorption band in the UV-visible region. The position of this band is strongly influenced by the structure of the compounds, for example by the type of substitution pattern in the donor and the acceptor moieties. Dramatic differences in energy occur upon tricyanovinyl-substitution of thienylpyrroles *2*. For example, thienylpyrrole *2e* (λ_{max} = 286.5 nm) is shifted 239 nm upon tricyanovinyl substitution (tricyanovinyl-pyrrole *1e*, λ_{max} = 525.5 nm) (Table 1, Figure 1). This effect has been attributed to the stabilization of LUMO by the electron-withdrawing groups [13]. The influence of the substituent on the nitrogen atom of the pyrrole ring is demonstrated by comparison of the absorption maxima of compounds *1a* and *1e* as the longest wavelength transition is shifted from 491.5 nm in pyrrole *1a* (Table 1, entry 1) to 525.5 nm for pyrrole *1e* (Table 1, entry 5). In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. According to Zyss [1] the increase of the β values characteristic of the NLO effects is

accompanied by an increase of the λ_{max} in the UV-visible spectra, i.e. a decrease in the intermolecular charge transfer (ICT) values.
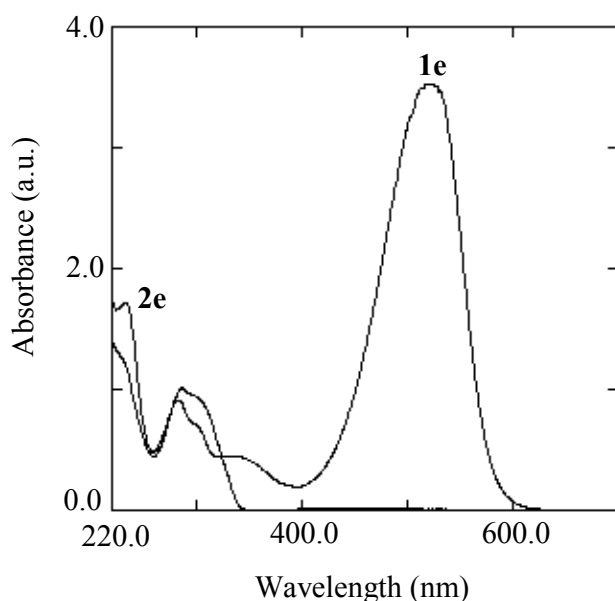

Figure 1 – UV-visible spectra of compounds *1e* and *2e* recorded in ethanol, demonstrating the effect of the tricyanovinyl- substitution of the pyrrole ring on the absorption maxima.

Solvatochromic study. To evaluate the intermolecular forces between the solvents and the solute molecules and in order to determine the best indicator dye, we made a preliminary study of the absorption spectra of compounds *1b-g* in 3 selected solvents of different solvatation character (diethyl ether, ethanol and DMF). We found that compound *1g* show the longest shift in wavenumber maxima ($\Delta\upsilon$ = + 804) cm^{-1} so a full solvatochromic study involving 14 solvents was carried out (Table 2). The maxima of the wavenumbers for compound *1g* measured in 14 solvents as well the corresponding wavelength λ are listed in Table 2 and compared the π^* determined by Kamlet and Taft [14].

Table 2- Solvatochromic data [λ_{max} (nm) and υ_{max} (cm^{-1}) of the charge-transfer band] for tricyanovinylpyrrole *1g* in various a solvents with π^* values by Kamlet and Taft [14]

Solvent[a]	π^*	λ_{max} [nm]	υ_{max} [cm^{-1}]
n-hexane	-0.08	502.5	19,900
ciclohexane	0.00	506.5	19,743
diethyl ether	0.27	513.0	19,493
ethyl acetate	0.55	513.0	19,493
toluene	0.54	519.5	19,249
ethanol	0.54	519.0	19,268
THF	0.58	517.0	19,342
methanol	0.60	520.0	19,231
acetone	0.71	518.0	19,305
acetonitrile	0.75	518.5	19,286
chloroform	0.76 [15]	525.5	19,029
dichloromethane	0.82	526.0	19,011
DMF	0.88	528.0	18,939
DMSO	1.00	533.5	18,744

[a]Solvent used as received.

The highest energy transitions are found with non polar solvents (cyclohexane). More polar solvents such as DMSO resulted in lower energy transitions. This behavior has been defined as a positive solvatochromic response that is related to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent. Because of the pronounced solvatochromism, the good correlation with π^* values for the 14 solvents investigated (r = 0.9419) and the long wavelength absorption in the visible range, *1g* seemed to be a very appropriate solvent polarity indicating dye. Noteworthy is the behavior of this compound in chlorinated solvents, which display the lowest energy transitions. Similar behavior has been observed for donor-acceptor substituted oligothiophenes where the trend was rationalized as a consequence of an intramolecular charge transfer [4, 16].

Electrochemical study. The redox properties of all tricyanovinyl-substituted thienylpyrroles *1* were investigated by cyclic voltammetry (Table 3). All compounds displayed one oxidative process under the experimental conditions. The precursors thienylpyrroles *2* showed an irreversible oxidation. Upon tricyanovinyl-substitution, the compounds display oxidation at more positive potentials as a consequence of the destabilizing effect of the electron-withdrawing tricyanovinyl group [17]. For example, pyrrole *2b* display an oxidation at $^1E_{1/2}$ = 0.48 V and the correspondent tricyanovinyl derivative *1b* display an oxidation at $^1E_{1/2}$ = 0.95 V. The tricyanovinyl-substituted thienylpyrroles display two reduction processes. For all compounds, the first process is stable on the cyclic voltammetry scale. An obvious cathodic shift of reduction peak potentials was observed with the increase of capacity of the donor group in the aryl moiety of pyrroles *1*. Electrochemical band gaps (Table 3), were calculated as described previously [18] from the onset potentials of the anodic and cathodic processes and agree well with the calculated optical band gaps. To our knowledge, these are some of the lowest band-gap materials based on thienylpyrrole derivatives.

Table 3- Electrochemical data for thienylpyrroles *2* and 5-tricyanovinyl-substituted thienylpyrroles *1* at a glassy carbon electrode.[a]

Thienylpyrroles		Tricyanovinyl-substituted thienylpyrroles				
Compound	Oxidation E_{pa} (V)	Compound	Oxidation E_{pa} (V)	Reduction $-^1E_{1/2}$ (V)	$-^2E_{pc}$ (V)	band gap[b] (eV)
2a	0.57	*1a*	1.11	0.92	1.61	1.95
2b	0.53	*1b*	0.95	1.00	1.70	1.89
2c	0.54	*1c*	0.96	1.02	1.73	1.91
2d	0.48	*1d*	0.94	1.14	1.80	2.01
2e	0.45	*1e*	0.92	1.05	1.75	1.88
2f	0.48	*1f*	0.95	1.01	1.78	1.88
2g	0.46	*1g*	0.94	1.06	1.72	1.94

[a] Solution approximately 1.5 mM in each compounds in acetonitrile 0.10 M [NBu$_4$][BF$_4$] was used, and the scan rate was 100 mV s^{-1}, potentials *versus* the ferrocinium/ferrocene-couple.

[b] E_{HOMO} = 4.80 + E_{ox} (eV) and E_{LUMO} = E_{red} + 4.80 (eV). The onset potentials were determined from the intersection of the two tangents drawn at the rising current and background charging currents of the CV´s.

Conclusions

In summary, we have synthesized tricyanovinyl-substituted thienylpyrroles *1* by direct tricyanovinylation reaction of thienylpyrroles *2* with TCNE in fair to good yields. Compounds *1* were characterized by elemental analysis and/or HRMS, ^{1}H and ^{13}C spectroscopy, IR and UV-Vis. spectroscopy. These materials exhibit dramatic changes in both their electronic and redox properties in comparison to the precursors thienylpyrroles. In agreement with the solvatochromic and the electrochemical studies and with previous findings [7-8] the new compounds prepared can be applied for the manufacture of materials with notable non-linear (NLO) properties.

Acknowledgements

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