New thienylpyrrolyl-cyanoacetic acid derivatives: synthesis and evaluation of the optical and solvatochromic properties

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Abstract: The novel thienylpyrrolyl-cyanoacetic acid derivatives were obtained in good yields through a simple Knoevenagel condensation of the corresponding precursor aldehydes with cyanoacetic acid in acetonitrile at reflux, using piperidine as catalyst. The formyl precursors **1-2** were obtained through two different methods: (i) lithiation followed by treatment with DMF and (ii) Suzuki cross-coupling reaction. The novel push-pull systems were completely characterized by the usual spectroscopic techniques and the optical and solvatochromic properties were evaluated.

Keywords: Thiophene; Pyrrole; Cyanoacetic acids; UV-visible spectroscopy; Solvatochromism; Fluorescence

1. Introduction

Among the organic molecules, the so-called push-pull or dipolar molecules (D-π-A) offer versatility of synthesis and ability to modulate their photophysical and photochemical properties. The cyanoacetic acid moiety has been used extensively as the acceptor group in D-π-A molecules motivated by its easy/inexpensive synthesis and ability to simultaneously act as a strong electron withdrawing moiety, as well as a stable anchoring group in dye-sensitized solar cells (DSSCs).[1] The capability of cyanoacetic acid derivatives to be used in efficient DSSCs is improved by its interesting properties, such as high power conversion, high structural flexibility and high molar absorption coefficients in the visible region [1a, 1b, 2]. Various π-conjugated bridging systems including aromatic and heteroaromatic rings have been introduced to induce efficient charge separation between D and A moieties. Thiophene and its oligomers are among the most frequently used π-conjugated bridges in push-pull molecules and are usually built by strong donor (D) and acceptor (A) groups connected by the highly conjugated thiophene-based π-spacer.

Our previous work on the synthesis and characterization of D-π-A chromophores in which the donor part (D) is represented by a π-excessive five-membered heteroaromatic system (pyrrole or thiophene) functionalized by electron donor groups and the acceptor part (A) is a strong electron acceptor group

("classical" or an electron-deficient heterocycle) has shown that they exhibit excellent solvatochromic, photochromic, emissive properties, good photovoltaic efficiencies, exceptional thermal stabilities and good to excellent nonlinear optical (NLO) response.[3] In this work, we report the synthesis of new D-π-A chromophores functionalized with cyanoacetic acid as acceptor group, linked to the thienylpyrrole heterocyclic system, which plays the dual role of π-bridge and auxiliary donor group.

2. Experimental

2.1. General

Reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was effected by silica gel column chromatography (Merck Kieselgel 60; 230–400 mesh). NMR spectra were obtained on a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C using the solvent peak as internal reference (δ relative to TMS and given in ppm). Mps were determined on a Gallenkamp apparatus. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. UV-vis absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Mass spectrometry analyses were performed at the "C.A.C.T.I. -Unidad de Espectrometria de Masas" at the University of Vigo, Spain. Formyl-thienylpyrrole precursors (**1-2**) were synthesized through a procedure described elsewhere.[4,5] Other reagents were of common commercial grade and were used as received.

2.2. General procedure for the synthesis of thienylpyrrolyl-cyanoacetic acid derivatives (3-4)

A solution of formyl-thienylpyrrole precursors (**1-2**) (0.19 mmol) and cyanoacetic acid (2.2 equiv, 0.42 mmol) and piperidine (3 drops) in acetonitrile (5 mL) was refluxed for 6 h. The mixture was cooled to room temperature and a few drops of aqueous HCl 1 M was added to induce precipitation. The formed precipitate was filtered and recrystalized from dichloromethane.

2-Cyano-3-(1'-propyl-5'-(thiophen-2''-yl)-1H-pyrrol-2'-yl)acetic acid (**3a**).

Compound **3a** was isolated as a yellow solid (49 %). Mp: 168.0–169.2 ºC. UV-vis (dioxane): λ_{max} nm (log ε) 406 (4.25). IR (liquid film): *v* 2215 (CN), 1681 (C=O), 1571, 1422, 1401, 1266, 1222, 1170, 1063 cm^{-1}. ^{1}H RMN (400 MHz, $CDCl_3$): δ 0.97 (t, 3H, *J*= 7.6 and 7.2 Hz, $CH_2CH_2CH_3$), 1.76–1.83 (m, 2H, $CH_2CH_2CH_3$), 4.20 (t, 2H, *J*= 8.0 and 7.6 Hz, $CH_2CH_2CH_3$), 6.61 (dd, 1H, *J*= 4.8 and 0.4 Hz, H-3), 7.17-7.19 (m, 1H, H-4'), 7.22 (dd, 1H, *J*= 3.6 and 1.2 Hz, H-3'), 7.49 (dd, 1H, *J*= 4.8 and 1.2 Hz, 5'-H), 7.89 (d, 1H, *J* = 4.4 Hz, H-4) 8.15 (s, 1H, =C*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ11.06 ($CH_2CH_2CH_3$), 25.51 ($CH_2CH_2CH_3$), 45.93 ($CH_2CH_2CH_3$), 90.99 (CH=*C*), 115.13 (C3), 116.89 (CN), 120.99 (C4), 127.72 (C5'), 127.91 (C3'), 127.96 (C4'), 128.34 (C2), 132.13 (C2'), 137.26 (C5), 140.15 (=*C*H), 168.89 (*C*OOH) ppm. MS: *m/z* (ESI, %): 287 ([M+H]$^{+}$, 100), 269 (16). HRMS: (ESI) *m/z* (%) for $C_{15}H_{14}N_2O_2S$: calcd 287.0857; found 287.0848.

2-Cyano-3-(5'-(1''-propyl-1H-pyrrol-2''-yl)thiophen-2'-yl)acetic acid (**4a**).

Compound **4a** was isolated as a red solid (65 %). Mp: 165.0–166.0 ºC. UV-vis (dioxane): λ_{max} nm (log ε) 440 (4.21). IR (liquid film): *v* 2215 (CN), 1685 (C=O), 1658, 1572, 1530, 1419, 1265, 1224, 1158, 1077 cm^{-1}. ^1H RMN (400 MHz, DMSO-d_6): δ 0.83 (t, 3H, *J* = 7.5 and 7.2 Hz, $CH_2CH_2CH_3$), 1.62–1.69 (m, 2H, $CH_2CH_2CH_3$), 4.11 (t, 2H, *J*= 7.2 Hz, $CH_2CH_2CH_3$), 6.14–6.16 (m, 1H, H-4'), 6.58 (dd, 1H, *J*= 3.9 and 2.1 Hz, H-5'), 7.07-7.09 (m, 1H, H-3'), 7.36 (d, 1H, *J*= 3.9 Hz, H-4), 7.94 (d, 1H, *J*= 3.9 Hz, H-3), 8.42 (s, 1H, =C*H*) ppm. ^{13}C NMR (100.6 MHz,DMSO-d_6): δ 11.75 ($CH_2CH_2CH_3$), 24.24 ($CH_2CH_2CH_3$), 49.10 ($CH_2CH_2CH_3$), 97.00 (CH=*C*), 108.82 (C4'), 112.71 (C5'), 116.97 (CN), 124.36 (C4), 124.99 (C2'), 127.16 (C3'), 132.76 (C2), 140.99 (C3), 144.28 (C5), 146.11 (=*C*H), 163.81 (*C*OOH) ppm. MS: *m/z* (ESI, %): 287 ($[M+H]^+$, 100), 177 (15), 163 (75). HRMS: (ESI) *m/z* (%) for $C_{15}H_{14}N_2O_2S$: calcd 287.0849; found 287.0849.

2-Cyano-3-(5'-(1''-phenyl-1H-pyrrol-2''-yl)thiophen-2'-yl)acetic acid (**4b**).

Compound **4b** was isolated as a dark red solid (62 %). Mp:180.0–181.0 ºC. UV-vis (dioxane): λ_{max} nm (log ε) 434 (4.24). IR (liquid film): *v* 2216 (CN), 1684 (C=O), 1575, 1534, 1498, 1420, 1315, 1266, 1241, 1210, 1148, 1069, 1043 cm^{-1}. ^1H RMN (400 MHz, DMSO-d_6): δ 6.37 (m, 1H, H-4'), 7.74 (d, 1H, *J*= 4.0 Hz, H-4), 6.80 (dd, 1H, *J*= 3.6 and 1.2 Hz, H-5'), 7.18 (m, 1H, H-3'), 7.34–7.37 (m, 2H, H-3'' and H-5''), 7.47–7.52 (m, 3H, H-2'', H-4'' and H-6''), 7.74 (d, 1H, *J*= 4.4 Hz, H-3), 8.30 (s, 1H, =C*H*), 13.54 (broad s, 1H, COO*H*) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 96.88 (CH=*C*), 110.28 (C4'), 113.36 (C5'), 116.47 (CN), 124.64 (C4), 126.15 (C2'), 126.92 (C3'' and C5''), 127.98 (C3'), 128.66 (C4''), 129.56 (C2'' and C6''), 132.88 (C2), 138.74 (C1''), 140.33 (C3), 144.22 (C5), 146.23 (=*C*H), 163.73 (*C*OOH) ppm. MS: *m/z* (EI, %): 320 (M^+, 6), 273 (100), 258 (10), 230 (36), 186 (22), 94 (18), 78 (47). HRMS: (EI) *m/z* (%) for $C_{18}H_{12}N_2O_2S$: calcd 320.0619; found 320.0620.

2-Cyano-3-(5'-(1''-(4'''-methoxyphenyl)-1H-pyrrol-2''-yl)thiophen-2'-yl)acetic acid (**4c**).

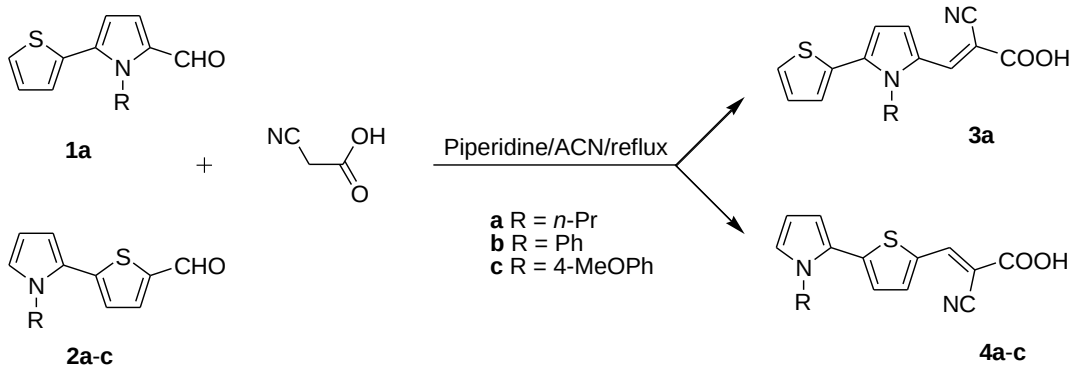
Compound **4c** was isolated as a dark red solid (50 %). Mp: 140.0–141.0 ºC. UV-vis (dioxane): λ_{max} nm (log ε) 440 (4.19). IR (liquid film): *v* 2214 (CN), 1684 (C=O), 1574, 1515, 1417, 1265, 1149, 1069, 1044 cm^{-1}. ^1H RMN (400 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 6.36 (m, 1H, H-4'), 6.69 (d, 1H, *J*= 4.4 Hz, H-4), 6.80 (dd, 1H, *J*= 4.0 and 1.6 Hz, H-5'), 6.94 (m, 1H, H-3'), 7.00 (dd, 2H, *J*= 8.8 and 2.0 Hz, H-3'' and H-5''), 7.24 (dd, 2H, *J*= 9.2 and 2.4 Hz, H-2'' and H-6''), 7.59 (d, 1H, *J*= 4.4 Hz, H-3), 8.16 (s, 1H, =C*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ55.63 (OCH_3), 94.65 (CH=*C*), 110.17 (C4'), 113.11 (C5'), 114.74 (C3'' and C5''), 115.96 (CN), 124.42 (C4), 127.37 (C2'), 128.05 (C3'), 128.37 (C2'' and C6''), 131.81 (C1''), 132.73 (C2), 138.92 (C3), 147.14 (C5), 147.40 (=*C*H), 160.07 (C4''), 167.13 (*C*OOH)

ppm. MS: *m/z* (EI, %): 350 (M^+, 5), 307 (46), 291 (45), 273 (24), 123 (24), 98 (33), 81 (82), 69 (100). HRMS: (EI) *m/z* (%) for $C_{19}H_{14}N_2O_3S$: calcd 350.0725; found 350.0721.

3. Results and discussion

3.1. Synthesis

The functionalization of thienylpyrrole moieties with the formyl group was performed through two methods: (i) the Vilsmeyer reaction [5] or by (ii) metalation followed by formyldelithiation using DMF [4-5, 6]. Formyl-thienylpyrroles **1a** and **2a-c** were used as precursors of cyanoacetic acids **3a** and **4a-c** in order to evaluate the effect of the position of cyanoacetic acid moiety on the optical properties of these chromophores. These push-pull conjugated chromophores **3a** and **4a-c** were synthesized by Knoevenagel condensation of the corresponding aldehyde precursors **1a** and **2a-c** with cyanoacetic acid in acetonitrile at reflux, using piperidine as catalyst (Scheme I, Table 1). The novel chromophores **3a** and **4a-c** were obtained in good yields (49–65%) and were completely characterized by the usual spectroscopic techniques (^{1}H and ^{13}C NMR, IR, HRMS and UV-vis).



Scheme I. Synthesis of thienylpyrrolyl-cyanoacetic acid derivatives **3a** and **4a-c**.

In the ^{1}H NMR spectra of cyanoacetic acids derivatives, signals at about 8.15–8.42 ppm were attributed to the vinylic =CH proton. A broad correlation could be observed between the donor properties of the thienylpyrrolyl system attached to the cyanoacetic acid group and the chemical shift of the vinylic =CH proton. In fact, from the data in table 1, one may infer that having cyanoacetic group attached to the pyrrole ring of the thienylpyrrole system (in compound **3a**, δ= 8.15 ppm) results in a decrease of the chemical shift of the vinylic =CH proton in the ^{1}H NMR spectra. On the contrary, for derivative **4a** having the cyanoacetic group attached to the thiophene ring of the thienylpyrrole system, a deshielding effect was observed (δ=8.53 ppm). As for the influence of the substituent groups in compounds **4a-c**, it could be seen that the higher the electron donating character of the substituent, the more shielded the vinylic proton appeared. This effect could be due to the donor effect of the propyl electron-donating group at the nitrogen atom of the pyrrole and also to the auxiliary donor strength of the heterocycle. In

the IR spectra the stretching bands of carboxylic C=O were observed as sharp bands at about 1681–1785 cm^{-1}. The CN stretching band was also identified at about 2214–2216 cm^{-1} (Table 1).

Table 1. Yields, UV-vis and IR absorption and ^{1}H NMR data of thienylpyrrolyl-cyanoacetic acids **3a** and **4a-c**.

Product	Yield (%)	UV-vis [a]		IR ν (cm^{-1})		δ_H (ppm)
		λ_{max} (nm)	log ε	CN	C=O	=C*H*
3a	49	406	4.25	2215	1681	8.15
4a	65	440	4.21	2215	1685	8.42
4b	62	434	4.24	2216	1684	8.30
4c	50	440	4.19	2214	1684	8.16

[a] Experimental spectroscopic data measured in 1,4-dioxane solution.

3.2. UV-vis absorption study of thienylpyrrolyl-cyanoacetic acids 3-4

The absorption spectra of thienylpyrrolyl-cyanoacetic acids **3a** and **4a-c** were measured in 1,4-dioxane (10^{-5} M solution) (Table 1). The position of the lowest energy charge-transfer band was extremely influenced by the electronic nature of the thienylpyrrole π-conjugated bridge and by the position of attachment of the cyanoacetic acid group (on the pyrrole or on the thiophene ring). As expected, the introduction of the cyanoacetic acid group at position 5 of thiophene (as in **4a**), relative to the same acceptor group at the same position of pyrrole (as in **3a**), resulted in a bathochromic shift of about 34 nm in the λ_{max} of absorption for **4a** (Table 1, Figure 1). This fact could be due to less steric hindrance and more extensive electron delocalization for compound **4a**.[3h,i]

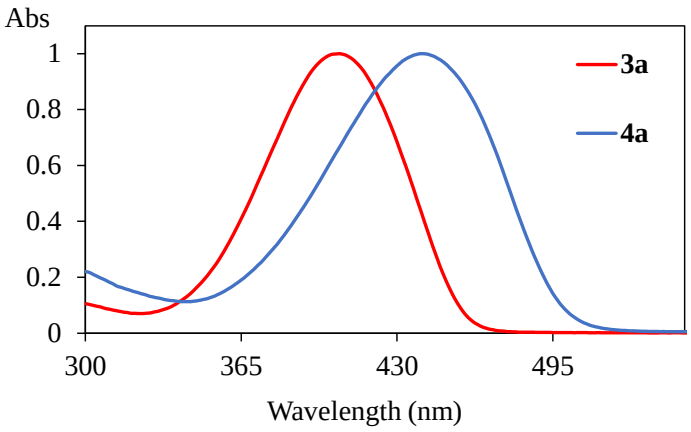


Figure 1. Normalized UV-vis absorption spectra of compounds **3a** and **4a** in 1,4-dioxane.

3.3. Solvatochromic study of cyanoacetic acids 3-4

To evaluate the electron transmission ability of thienylpyrrolyl-cyanoacetic acids **3-4** with the increase of solvent polarity, the UV-vis absorption spectra were measured in 5 solvents with different solvation character (diethyl ether, ethanol, dioxane, chloroform and DMSO) and their wavelengths of maximum absorption compiled in Table 2. Compound **4b** exhibited positive solvatochromism ($\Delta\nu_{max}$ = +270 cm^{-1}) with respect to its CT absorption band, that is, the progressive red shift of the lowest energy absorption as the polarity of the solvent increases due to a greater stabilization of the excited state relative to the ground state, concomitant with a declining of the transition energy (band gap). On the other hand, a negative solvatochromism was observed for compounds **3a** ($\Delta\nu_{max}$ = -1620 cm^{-1}), **4a** ($\Delta\nu_{max}$ = -378 cm^{-1}), and **4c** ($\Delta\nu_{max}$ = -2339 cm^{-1}) (see Table 2).

In view of the noticeable solvatochromism, the good correlation with π* values for the 5 solvents investigated and the long wavelength absorption in the visible range, compound **4c** appears to be a good solvatochromic probe.

Table 2. Solvatochromic data [λ_{max} (nm) and $\Delta\nu_{max}$ (cm^{-1}) of the charge-transfer band] for thienylpyrrolyl-cyanoacetic acids **3-4** in 5 selected solvents with π* values by Kamlet and Taft [7].

Cpd	Diethyl ether (0.27) λ_{max}	Ethanol (0.54) λ_{max}	Dioxane (0.55) λ_{max}	Chloroform (0.76) λ_{max}	DMSO (1.00) λ_{max}	$\Delta\nu_{max}$ (cm^{-1})[a]
3a	397	387	406	412	373	-1620
4a	434	416	440	448	427	-378
4b	428	403	434	440	433	+270
4c	434	408	440	448	394	-2339

[a] $\Delta\nu_{max} = \nu_{max\ (diethyl\ ether)} - \nu_{max\ (DMSO)}$.

4. Conclusions

Novel thienylpyrrolyl-cyanoacetic acids **3-4** were synthesized in good yields (49–65%) from easily available formylated precursors **1-2** and low cost commercially available reagents, through a simple Knoevenagel condensation, using piperidine as catalyst. The donor-acceptor π-conjugated cyanoacetic acids **3-4** showed excellent solvatochromic properties, and seem to be very appropriate solvent polarity indicating dyes.

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