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Synthesis and Characterization of Dicyanovinyl-Substituted Thienylpyrroles as New Nonlinear Optical Chromophores

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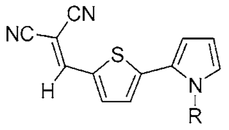
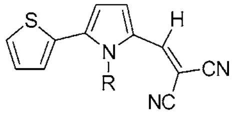
ABSTRACT



2a$_1$, 2 b-e R = alkyl or aryl



2a$_2$ R = alkyl

New dicyanovinyl-substituted 1-(alkyl)aryl-2-(2′-thienyl)pyrroles 2 were synthesized and characterized. The solvatochromic behavior of the synthesized compounds was investigated. All the derivatives showed reversible oxidation and reduction on the CV time scale. The hyperpolarizabilities (β) of compounds 2 were measured using hyper-Rayleigh scattering. The results are among the highest β values reported for donor–acceptor-substituted thienylpyrroles.

The electronic and structural properties of donor−acceptor-substituted conjugated organic compounds are of considerable interest because of their potential applications in a variety of electrooptic devices.[1] A wide range of structural modifications to the donor, acceptor, and π-conjugated moieties have been carried out.[2] Synthetic[3] and theoretical[4] studies have demonstrated that replacing the benzene ring of a chromophore bridge with easily delocalizable five-membered heteroaromatic rings, such as thiophene, pyrrole, and thiazole, results in an enhanced molecular hyperpolarizability of donor−acceptor compounds. Although the aromaticity of heteroaromatics affects the electron transfer between donor and acceptor groups, the electron-excessive or electron-deficient nature of the heterocyclic ring systems may also play a major role in determining the overall electron-donating and -accepting ability of the substituents.[5] Conjugated thiophene and pyrrole derivatives as donors

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(1) (a) Zyss, J. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1994. (b) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991; pp 132−174. (c) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (d) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: New York, 1997. (e) Meyers, F.; Marder, S. R.; Perry, J. W. In *Chemistry of Advanced Materials: An Overview*; Interrante, L. V., Hampden-Smith, M. J., Eds.; Wiley-VCH: New York, 1998; pp 207−269.

(2) (a) Cheng, L. T.; Tam, W.; Marder, S. R.; Steigman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643. (b) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jenand, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060. (c) Wong, M. S.; Bosshard, Ch.; Pan, F.; Gunter, P. *Adv. Mater.* **1996**, *8*, 677. (d) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem.−Eur. J.* **1997**, *3*, 1091.

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substituted with appropriate acceptor groups are promising candidates among such push−pull systems.[6]

Recently, several authors have reported the synthesis and characterization of chromophores in which the donor moiety is represented by a π-excessive five-membered heterocycle (pyrrole or thiophene) and the acceptor group is a deficient heterocyclic azine ring (pyridine, pyrazine, pyrimidine, pyridazine), which exhibit solvatochromic, electrochromic, photochromic, fluorescent, and nonlinear optical properties.[3f−h,7]

During the last years, we have investigated several donor−acceptor-substituted heterocyclic compounds including oligothiophenes,[8] benzothiazoles,[9] thienylphthalazines,[10] and thienylpyrroles.[11] In particular, thienylpyrrole derivatives which typically exhibit favorable solvatochromic, electrochemical, photochromic, and nonlinear optical (NLO) properties could be used in the manufacturing of semiconductor materials, in optical data storage devices and second-harmonic generators. We were therefore motivated to explore the potential of conjugated 1-(alkyl)aryl-2-(2′-thienyl)pyrroles as strong π-electron-donor moieties functionalized with the dicyanovinyl group on the thiophene or on the pyrrole moiety, examples of which as far as we are aware have not yet been reported in the literature. In this report, we present the synthesis, UV−vis, solvatochromic, redox, and second-order NLO properties of new thienylpyrrole-containing chromophores with a dicyanovinyl acceptor on the thiophene or pyrrole ring.

Scheme 1

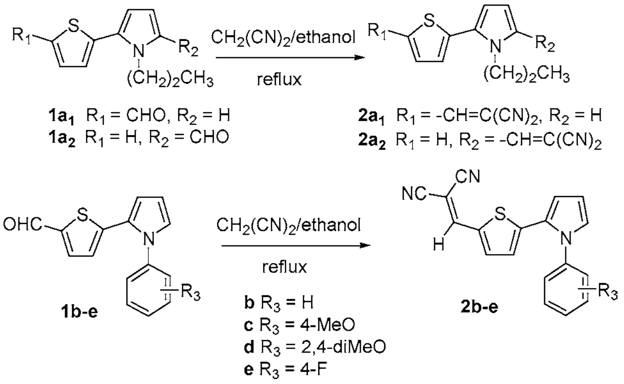

Table 1. Experimental Data for **1** and **2**

compd	λ_{max} (nm)[a]	compd	yield (%)	λ_{max} (nm)[a]	δ_H (ppm)[b]	IR υ_{CN} (cm^{-1})
1a$_1$	374.0	**2a$_1$**	93	454.5	7.75	2215
1a$_2$	321.5	**2a$_2$**	100	415.0	7.46	2217
1b	374.0	**2b**	47	455.0	7.61	2219
1c	379.0	**2c**	100	462.0	7.59	2215
1d	384.5	**2d**	90	473.5	7.57	2217
1e	373.5	**2e**	36	454.5	7.62	2217

[a] All the UV−vis spectra were run in ethanol. [b] For the −C*H*=C(CN)$_2$ proton of thienylpyrroles **2** (300 MHz, CDCl$_3$).

Recently, we have developed a method for the synthesis of formylthienylpyrroles **1**.[11d] Knoevenagel condensation of aldehydes **1** with malononitrile[12] in refluxing ethanol gave dicyanovinyl derivatives **2** (Scheme 1, Table 1) in moderate to excellent yields (36−100%). To compare the electrochemical and the optical properties of dicyanovinyl-pyrroles **2** with the dicyanovinyl group substituted on the pyrrole or thiophene ring, we have synthesized compounds **2a$_1$** and **2a$_2$** from the corresponding formyl derivatives **1a$_1$** and **1a$_2$**. The structures of dicyanovinyl-substituted pyrrole derivatives **2**

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(3) (a) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1993**, *34*, 1747. (b) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun*. **1993**, 90. (c) Rao, V. P.; Jen, W. K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118. (d) Chou, S.-S. P.; Sun, D.-J.; Lin, H.-C.; Yang, P.-K. *Tetrahedron Lett.* **1996**, *37*, 7279. (e) Shu, C.-F.; Tsai, W.-J.; Chen, J.-Y.; Jen, A. K.-Y.; Zhang, Y.; Chen, T.-A. *J. Chem. Soc., Chem. Commun*. **1996**, 2279. (f) Facchetti, A.; Abbotto, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Marks, T. J.; Pagani, G. A. *Chem. Mater*. **2002**, *14*, 4996. (g) Facchetti, A.; Abbotto, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Pagani, G. A.; Marks, T. J. *Chem. Mater*. **2003**, *15*, 1064. (h) Facchetti, A.; Beverina, L.; van der Boom, M. E.; Dutta, E. G.; Pagani, G. A.; Marks, T. J. *J. Am. Chem. Soc*. **2006**, *128*, 2142 and references therein.

(4) (a) Varanasi, P. R.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443. (b) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575. (c) Breitung, E. M.; Shu, C.-F.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1154.

(5) (a) Gilchrist, T. L. *Heterocyclic Chemistry*; Wiley: New York, 1985. (b) Shu, C.-F.; Wang, Y.-K. *J. Mater. Chem.* **1998**, *8*, 833. (c) Wang, Y.-K.; Shu, C.-F.; Breitung, E. M.; McMahon, R. J. *J. Mater. Chem*. **1999**, *9*, 1449.

(6) (a) Kotkar, D.; Joshi, V.; Ghosh, P. K. *J. Chem. Soc., Chem. Commun.* **1988**, 917. (b) Lucchesini, F. *Tetrahedron* **1992**, *48*, 9951. (c) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. *J. Org. Chem.* **1993**, *58*, 904. (d) Pagani, G. A. *Heterocycles* **1994**, *37* (3), 2069. (e) Parakka, J. P.; Cava, M. P. *Synth. Met.* **1995**, *68*, 275. (f) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (g) Korostova, S. E.; Mikhaleva, A. I.; Trofimov, B. A. *Russ. Chem. Rev. (Engl. Transl.)* **1999**, *68* (6), 459 and references therein. (h) Just, P. E.; Chane-Ching, K. I.; Lacaze, P. C. *Tetrahedron* **2002**, *58* (18), 3467. (i) Ono, K.; Totani, H.; Ohkita, M.; Saito, K.; Kato, M. *Heterocycles* **2004**, *64* (1), 223. (j) Zotti, G.; Zecchin, S.; Schiavon, G.; Vercelli, B.; Berlin, A.; Grimoldi, S. *Macromol. Chem. Phys.* **2004**, *205*, 2026 and references therein. (k) Ogura, K.; Ooshima, K.; Akazome, M.; Matsumoto, S. *Tetrahedron* **2006**, *62* (11), 2484 and references therein.

(7) (a) Bradamante, S.; Facchetti, A.; Pagani, G. A. *J. Phys. Org. Chem.* **1997**, *10*, 514. (b) Abbotto, A.; Beverina, L.; Bradamante, S.; Facchetti, A.; Klein, C.; Pagani, G. A.; Redi-Abshiro, M.; Wortmann, R. *Chem.−Eur. J.* **2003**, *9*, 1991. (c) Abbotto, A.; Beverina, L.; Bradamante, S.; Faccheti, A.; Pagani, G. A.; Bozio, R.; Ferrante, C.; Pedron, D.; Signorini, R. *Synth. Met.* **2003**, *14*, 4996. (d) Thompson, B. C.; About, K. A.; Reynolds, J. R.; Nakatani, K.; Audebert, P. *New J. Chem.* **2005**, *29*, 1128. (e) Trofimov, B. A.; Vasil'tsov, A. M.; Schmidt, E. Y.; Zorina, N. V.; Afonin, A. V.; Mikhaleva, A. I.; Petrushenko, K. B.; Ushakov, I. A.; Krivdin, L. B.; Belsky, V. K.; Bryukvina, L. I. *Eur. J. Org. Chem.* **2005**, 4338.

(8) (a) Raposo, M. M. M.; Kirsch, G. *Heterocycles* **2001**, *55* (8), 1487. (b) Raposo, M. M. M.; Kirsch, G. *Tetrahedron* **2003**, *59* (26), 4891. (c) Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2004**, *60* (18), 4071.

(9) Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M. M. *Tetrahedron Lett.* **2004**, *45* (13), 2825.

(10) Raposo, M. M. M.; Sampaio, A. M. B. A.; Kirsch, G. *J. Heterocyc. Chem.* **2005**, *42* (7), 1245.

(11) (a) Raposo, M. M. M.; Sampaio, A. M. B. A.; Kirsch, G. *Synthesis* **2005**, *2*, 199. (b) Raposo, M. M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2005**, *61* (34), 8249. (c) Raposo, M. M. M.; Sousa, A. M. R. C.; Kirsch, G.; Ferreira, F.; Belsey, M.; Matos Gomes, E.; Fonseca, A. M. C. *Tetrahedron* **2005**, *61* (50), 11991. (d) Raposo, M. M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2006**, *62* (15), 3493. (e) Coelho, P. J.; Carvalho, L. M.; Fonseca, A. M. C.; Raposo, M. M. M. *Tetrahedron Lett.* **2006**, *47* (22), 3711.

(12) *Comprehensive Organic Synthesis*; Trost B. M., Ed.; Pergamon Press: Oxford, 1991; Coll. Vol. 2, pp 358−359.

were unambiguously confirmed by their analytical and spectral data.

The electronic spectra of dicyanovinyl-thienylpyrrole derivatives **2** dissolved in ethanol were recorded (Table 1). As expected, as the acceptor strength of the dicyanovinyl group in compounds **2** increases, correspondingly larger bathochromic shifts of the peak absorption wavelength, $\lambda_{\max}$, in the UV−vis spectra (Table 1) are observed. The position of the absorption bands is influenced by the structure of the compounds, for example, by the group that substitutes the nitrogen atom of the pyrrole ring or by the position of the substitution by the dicyanovinyl group on the pyrrole or thiophene ring. The influence of the position of the dicyanovinyl group on the pyrrole or on the thiophene ring on the absorption peak ($\lambda_{\max}$) for derivatives $\mathbf{2a_1}$−$\mathbf{2a_2}$ is noteworthy. As expected, the introduction of the dicyanovinyl group at the 5′-position of the thiophene ring ($\mathbf{2a_1}$), relative to the same acceptor group in the 5-position of the pyrrole ring ($\mathbf{2a_2}$), results in a bathochromic shift in the $\lambda_{\max}$ of absorption for $\mathbf{2a_1}$ due to more extensive electron delocalization.

Donor−acceptor-substituted thienylpyrroles have been known to demonstrate strong solvatochromic behavior.[11b,c] To determine the best indicator dye, we carried out a preliminary study of the absorption spectra for compounds **2** in solvents with different polarities (hexane, ethyl acetate, and DMF). We found that compounds $\mathbf{2a_1}$ ($\Delta\nu = +1085$ cm^{-1}) and **2d** ($\Delta\nu = +1156$ cm^{-1}) showed the largest energy shifts in the peak absorption band, so a full solvatochromic study involving 15 solvents was carried out. The results are summarized in Table 2.

Table 2. Solvatochromic Data [$\lambda_{\max}$ (nm) of the Charge-Transfer Band] for Compounds $\mathbf{2a_1}$ and **2d** in Selected Solvents

solvent[a]	π^* [13]	$\mathbf{2a_1}$ $\lambda_{\max}$(nm)	$\nu_{\max}$ (cm^{-1})	**2d** $\lambda_{\max}$(nm)	$\nu_{\max}$ (cm^{-1})
n-hexane	−0.08	449.0	22 272	498.5	20 060
cyclohexane	0.00	451.0	22 173	500.0	20 000
diethyl ether	0.27	455.0	21 978	507.5	19 704
toluene	0.54	461.0	21 692	513.0	19 493
ethanol	0.54	461.5	21 668	514.5	19 436
ethyl acetate	0.55	458.0	21 834	515.0	19 417
dioxane	0.55	460.0	21 739	514.0	19 455
THF	0.58	462.5	21 622	517.0	19 342
methanol	0.60	463.0	21 598	518.5	19 286
acetone	0.71	465.0	21 505	521.0	19 194
acetonitrile	0.75	467.0	21 413	524.0	19 084
chloroform	0.76[14]	471.0	21 231	531.0	18 832
DCM	0.82	472.5	21 164	532.0	18 797
DMF	0.88	469.0	21 322	529.0	18 904
DMSO	1.00	473.0	21 142	532.0	18 797

[a] Solvent used as received. [b] The correlation coefficient r obtained for the linear solvation energy relationship with π^* values by Kamlet and Taft without chlorinated solvents was $r = 0.9813$ for $\mathbf{2a_1}$ and $r = 0.9883$ for **2d**.

Compounds $\mathbf{2a_1}$ ($\Delta\upsilon = +1130$ cm^{-1}) and **2d** ($\Delta\upsilon = +1263$ cm^{-1}) exhibit positive solvatochromism with respect to their CT absorption band; that is, the position of the absorption maximum shifts to longer wavelengths as the polarity of the solvent increases. Noteworthy is the behavior of $\mathbf{2a_1}$ and **2d** in chlorinated solvents such as chloroform and dichloromethane, which display the lowest-energy transitions.[8c] In view of the pronounced solvatochromism, the good correlation with π^* values for the 15 solvents investigated and the long-wavelength absorption in the visible range, $\mathbf{2a_1}$, and **2d** appear to be quite reliable solvent polarity indicating dyes.

The redox properties of the dicyanovinyl-thienylpyrroles **2** were investigated by cyclic voltammetry, and the results are presented in Table 3.

Table 3. Electrochemical Data for Compounds **2**[a]

	oxidation			
compd	$E_{1/2}$ (V)	E_{pa} (V)	reduction $-E_{1/2}$ (V)	band gap[b] (eV)
$\mathbf{2a_1}$	0.46	0.96	1.56	2.02
$\mathbf{2a_2}$	0.80	1.20	1.46	2.26
2b	0.68	1.10	1.42	2.10
2c	0.59	1.06	1.44	2.03
2d	0.50	0.93	1.49	1.99
2e	0.56	1.00	1.47	2.03

[a] Measurements made in dry acetonitrile at a carbon working electrode with a scan rate of 0.1 V s^{-1}. All E values are quoted in volts vs the ferrocinium/ferrocene couple. [b] $E_{\mathrm{HOMO}} = 4.39 + E_{\mathrm{ox}}$ (eV) and $E_{\mathrm{LUMO}} = E_{\mathrm{red}} + 4.39$ (eV).

All compounds displayed two oxidative processes under the experimental conditions. A reversible process can be attributed to the formation of the radical cation of the pyrrole, whereas the extraction of subsequent electrons gives rise to an irreversible process. Upon dicyanovinylation, the compounds $\mathbf{2a_1}$ and **2b**−**e** display the first oxidation at about 0.46−0.68 V as a consequence of the destabilizing effect of the electron-withdrawing dicyanovinyl group.[11b,c,15] As the HOMO levels in the dicyanovinyl-thienylpyrroles **2** increase along the series with the donor strength of the nitrogen substitute in the pyrrole ring, the propensity for oxidation gradually decreases. Cyclic voltammetry shows that the reduction of thienylpyrroles **2** is a reversible one-electron process. The one-electron stoichiometry for these oxidation processes is ascertained by comparing the current heights with known one-electron redox processes under identical conditions.[11b,c] A clear cathodic shift of reduction peak potentials was also observed with an increase of the donor strength in the substitute group for nitrogen on the pyrroles. Electrochemical band gaps (Table 3) were calculated as described previously[11c,16] from the potentials of the anodic

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(13) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(14) Kamlet, M. J.; Abboud, J.-L M.; Abraham, M. H.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(15) (a) McCormac, T.; Farrell, D. *Electrochim. Acta* **2001**, *46*, 3287. (b) Dworczak, R.; Fabian, W. M. F. *Dyes Pigm*. **2002**, *53*, 119.

(16) Pei, J.; Ni, J.; Zhou, X. H.; Cao, X. L.; Lai, Y. H. *J. Org. Chem.* **2002**, *67*, 8104.

Table 4. UV−Vis Absorptions and β and β_0 Values for pNA, for Compounds **2**[a] and **3**[11c]

compd	$\lambda_{\max}$ (nm)	$\beta^b/10^{-30}$ esu	$\beta_0{}^c/10^{-30}$ esu	compd	$\lambda_{\max}$ (nm)	$\beta^b/10^{-30}$ esu	$\beta_0{}^c/10^{-30}$ esu
2a$_1$	458	526	111				
2a$_2$	414	85	28	**3a**	486	254	30
2b	450	364	85	**3b**	504	244	19
2c	458	439	93	**3c**	510	253	17
2d	514	651	33	**3d**	514	263	13
2e	449	439	104	**3e**	506	290	21
pNA	352	16.9[22,23]	8				

[a] Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions. [b] All the compounds are transparent at the 1064 nm fundamental wavelength. [c] Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta[1 - (\lambda_{\max}/1064)^2][1 - (\lambda_{\max}/532)^2]$; damping factors were not included.[19−21]

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.

We have used the hyper-Rayleigh scattering (HRS) method[17,18] to measure the first hyperpolarizability, β, of the dicyanovinyl derivatives **2**. *p*-Nitroaniline (pNA) was used as a standard to obtain quantitative values, whereas care was taken to properly account for possible fluorescence of the dyes. The static hyperpolarizability, β_0, values are calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution. The β values for compounds having the dicyanovinyl group on the thiophene ring are 22−38 times greater than pNA, whereas the respective β_0 values are 4−14 times greater. As expected, the β values for pyrroles **2b**−**d** increase with the donor strength of the group that substitutes the nitrogen atom on the pyrrole ring along the series Ph < 4-OMe-phenyl < 2,4-diOMe-Ph. Comparison of the β values for **2a$_1$** (526×10^{-30} esu) and **2a$_2$** (85×10^{-30} esu) shows that the substitution using the dicyanovinyl group at the 5′-position on the thiophene ring leads to a larger nonlinearity than the same acceptor group at the 5-position on the pyrrole ring (**2a$_2$**) (Table 4).

These results are in accordance with the theoretical studies of Varanasi et al. where it was concluded that the increase or decrease of the molecular nonlinear activity on heteroaromatic systems depends on the nature of the aromatic rings as well as on the location of these heteroaromatic rings in the systems.[4a] Recently, using the same method described above, we have studied the NLO properties of the tricyanovinyl-pyrroles **3** having the acceptor group substituted on the pyrrole moiety (Table 4, Figure 1).[11c] The results obtained showed that even with a stronger acceptor group these derivatives exhibit lower hyperpolarizability values compared with dicyanovinyl compounds **2a$_1$** and **2b**−**e**. Thus, the location of the dicyanovinyl group on the pyrrole or on the thiophene ring alone can either dramatically enhance or decrease the overall molecular nonlinearity of the system. One must therefore view the thienylpyrrole moiety not only as the conjugated segment but also as the structural unit, which affects the overall electron-transfer properties of the system. Pyrrole, being the most electron-rich five-membered heteroaromatic ring, counteracts the electron-withdrawing effect of the dicyanovinyl group (in **2a$_2$**), resulting in a decrease in β. The same explanation could be used to account for the lowest β values observed in tricyanovinyl-pyrroles as discussed earlier. As expected, the dicyanovinyl-pyrrole **2a$_2$** exhibits a lower value of β (85×10^{-30} esu) compared to 1-propyl-2-(-2′-thienyl)-5-tricyanovinyl-pyrrole (254×10^{-30} esu).[11c]

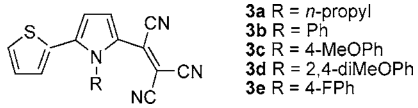

Figure 1. Structure of compounds **3**.

In summary, we have synthesized new dicyanovinyl-substituted thienylpyrroles **2** in moderate to excellent yields. To our knowledge, it is the first time that thienylpyrroles functionalized with an acceptor group on the thiophene ring are reported. These compounds exhibit a positive solvatochromic behavior and stable redox processes. These properties coupled with the excellent nonlinear optical properties make them promising candidates for NLO applications.

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Supporting Information Available: Experimental procedures, characterization data including ^{1}H and ^{13}C NMR spectral data of compounds, and electrochemical and nonlinear optical instrumental conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285.
(18) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.
(19) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.
(20) Oudar J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.
(21) Zyss, J.; Oudar, J. L. *Phys. Rev. A* **1982**, *26*, 2016.
(22) Teng, C. C.; Garito, A. F. *Phys. Rev. B* **1983**, *28*, 6766.
(23) Stahelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245.