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Synthesis, characterization and optical properties of merocyanines derived from malononitrile dimer

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Abstract—The reaction between malononitrile dimer and 1,3-dithiole-derived polyenals affords push–pull systems with (Z)-geometry around the newly formed C=C bond. In one instance, an unexpected shortening of the merocyanine chain takes place. These push–pull derivatives have weakly alternated structures and moderate optical nonlinearities, which can be modified by functionalization of the amino group.
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2-Amino-1,1,3-tricyanopropene (malononitrile dimer, **1**)[1,2] is a multifunctional molecule with a rich chemistry, which has allowed the preparation of new dyes[3,4] and chromoionophores,[5] among many other structures. To that end, the reactivity of **1** towards aromatic aldehydes has been widely explored,[3,5–8] whereas heterocyclic aldehydes have only seldom been used,[4,9,10] and there are very few examples of Knoevenagel reactions of **1** with α,β-unsaturated aldehydes.[4,11] Moreover, polycyano acceptor groups have been widely used in the search for new compounds with second-order nonlinear optical (NLO) properties,[12,13] and **1** is structurally related to the very successful acceptor 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF),[14] but, unlike the latter compound, the NLO properties of merocyanines derived from **1** have received a very limited attention.[7,8,11]

In this Letter, we report the synthesis and full stereochemical characterization of push–pull compounds **2** (Fig. 1), bearing a proaromatic 1,3-dithiole donor unit,[15,16] along with their electrochemical, linear and nonlinear optical properties. The latter are compared to those of related merocyanines bearing other polycyano acceptors.

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2: R = Me; **2'**: R = H
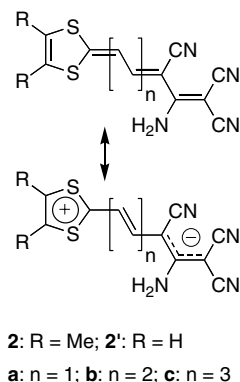**a**: n = 1; **b**: n = 2; **c**: n = 3

Figure 1.

The Knoevenagel reaction of **1** with aldehydes **3a**–**b**[17,18] afforded the expected products (**2a**–**b**)[19,20] in medium yields (Scheme 1).

Furthermore, compound **2a** was also prepared in higher yield[21] through the reaction of **1** with the recently reported iminium salt **4**,[22] which, as expected, behaves as an activated equivalent of aldehyde **3a**. On the other hand, the reaction of **1** with aldehyde **3c**[18] turned out to be more complex than anticipated, since it afforded a 4:1 mixture of **2c** and the unexpected product **2b** (Scheme 2), from which **2c** could be isolated by HPLC.[23]
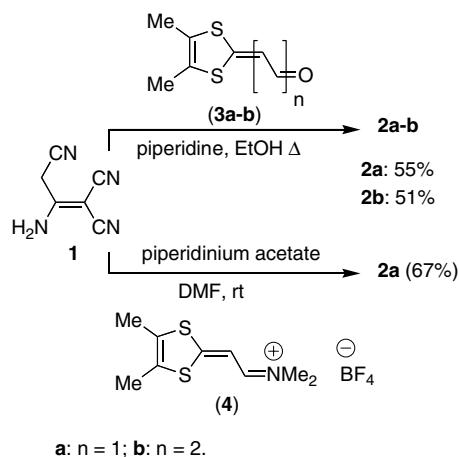
Scheme 1.
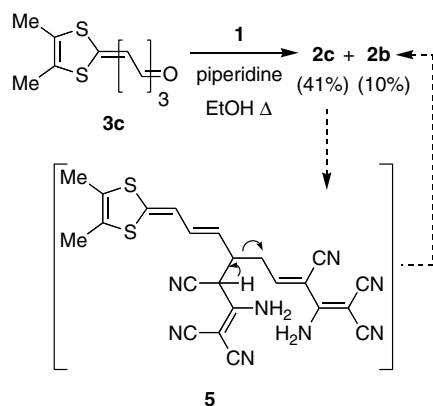
Scheme 2.

After reconfirming the purity of **3c**, a literature search revealed that the degradation of cyanines with a concomitant shortening of the conjugated chain was described long time ago.[24,25] Although the mechanism of this degradation is not clearly established, it seems that a nucleophilic attack on one of the electrophilic odd numbered carbon atoms of the cyanine plays a key role. Therefore, a tentative mechanism for the conversion of **2c** to **2b** could involve intermediate **5**, formed by Michael addition of the conjugated base of **1** to the appropriate carbon atom of **2c**. To the best of our knowledge, this is the first example of a reaction where a 'degradated' merocyanine (lacking a =CH–CH= group) is formed along with the expected one.

The Knoevenagel reaction of **1** with aldehydes can give rise to (Z)- and/or (E)-isomers and, except for the very few cases where X-ray diffraction data are available,[26,27] no effort has been described to structurally characterize the resulting compounds, although a (Z)/(E) mixture has been reported in one case.[7]

The geometries of compounds **2** in solution were determined by ^{1}H NMR studies. Unambiguous stereochemical assignment of the HC=CH bonds ((E)-configuration) and the HC–CH bonds (s-trans conformation) was possible thanks to $^3J_{HH}$ coupling constants analysis

along the polyenic chain. Moreover, NOE and NOESY experiments allowed the determination of the stereochemistry of the HC=C(CN) and the (H₂N)C–C(CN) bonds, showing that the C=C bond formed in the Knoevenagel reaction has (Z)-geometry, and that all C–C bonds along the spacer are s-trans. These stereochemical features are also found in the B3P86/6-31G* optimized geometries in the gas phase of model compounds **2′a–c** (Fig. 1) and in the previously mentioned X-ray diffraction studies.[26,27]

$^3J_{HH}$ values along the spacer (Table 1) provide some information about the ground state polarization of these merocyanines; thus, coupling constants of ca. 12 Hz and 13–14 Hz for the HC–CH and HC=CH bonds, respectively (as depicted in the neutral limiting form, Fig. 1), point to a contribution of the zwitterionic limiting form to the ground state of these molecules.

Both theoretical calculations and ^{1}H NMR data show that this partially zwitterionic character is more pronounced for the shorter derivatives. Thus, on going from **2′a** to **2′c**, Mulliken charges on the dithiole moiety decrease, whereas averaged SC–S bond lengths and BLA (bond length alternation along the spacer)[28] values increase. This trend is also mirrored by average ΔJ values,[29a] calculated as the difference between the averaged $^3J_{HH}$ values of the formally double and single bonds along the polymethine chain (e.g., for **2b**, $\Delta J = 13.1 - (11.9 + 12.4)/2 \approx 1.0$), which also increase on lengthening the π-spacer. Taken together, these data point to weakly alternated structures (BLA ≈ 0.04 Å, $\Delta J \leqslant 2.2$ Hz) when compared to all-trans polyenes (BLA ≈ 0.11 Å, $\Delta J \approx 6$ Hz).[29]

Electrochemical data of the newly prepared compounds are gathered in Table 2. All compounds show two chemically irreversible waves, corresponding to the oxidation of the dithiafulvene fragment and to the reduction of the acceptor moiety, respectively. An increase in the length of the polyenic spacer gives rise to both easier oxidation and reduction processes, thus revealing that a less effective electron withdrawal (donation) is felt by the donor (acceptor) fragment on passing from **2a** to **2c**. These observations point to a weaker interaction of the end groups (and, therefore, a smaller contribution of the zwitterionic form to the ground state for the longer derivatives), in good agreement with the results of theoretical calculations.

Table 1. ^{1}H NMR data and B3P86/6-31G* calculated values

Compound	$^3J_{HH}$[a,b]	ΔJ[a]	Dithiole charge[c]	SC–S[c,d]	BLA[c,d]
2a	12.6	—	+0.17	1.754	0.037
2b	11.9, 13.1, 12.4	1.0	+0.14	1.757	0.043
2c	11.7, 14.0, 11.7, 14.0, 11.9	2.2	+0.12	1.759	0.045

[a] In Hz in DMSO.
[b] Along the polymethine chain. From left to right: dithiole to acceptor end.
[c] Calculated for compounds **2′**.
[d] In Å.

Table 2. Electrochemical, linear and nonlinear optical properties

Compound	E_{ox}[a]	E_{red}[a]	λ_{max}[b]	$\mu\beta$[c]	$\mu\beta_0$[d]
2a	1.10	−1.00	520	165	107
2b	0.80	−0.86	541	690	430
2c	0.65	−0.75	564	1340	796

[a] E in V versus Ag/AgCl, glassy carbon working electrode, TBAPF$_6$
0.1 M in CH$_2$Cl$_2$, 0.1 V/s.
[b] In nm, measured in DMSO.
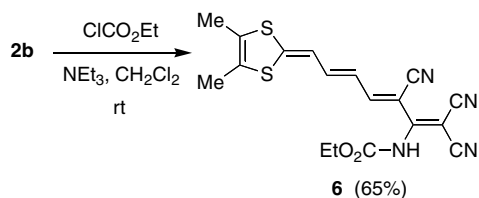[c] In 10^{-48} esu, measured in DMSO at 1907 nm.
[d] In 10^{-48} esu, determined using the two-level model.

The target compounds show moderate second-order NLO properties (EFISH measurements) with $\mu\beta_0$ values increasing with the conjugation path. A comparison with structurally related derivatives reveals that the effect of the 2-amino-1,3,3-tricyanopropenylidene group on the quadratic response is similar to that of the dicyanomethylene acceptor.[30,31]

Compounds **2a–c** show intense absorption bands in the visible region, which are bathochromically shifted on lengthening the π-spacer. It is worth noting that λ_{max} values of **2a–c** are blue-shifted when compared to those of other dithiole–π–acceptor compounds showing comparable hyperpolarizability values.[32,33] No doubt, this is related to the attachment of the electron-donating –NH$_2$ group to an odd-numbered position of the polymethine chain.[34] This kind of attachment is directly comparable to that of the oxygen atom present in the TCF moiety, the role of which was once considered unclear.[35] Given the very strong electron withdrawing character of the TCF fragment it now seems clear that the inductive effect of the oxygen atom is superior to its resonance effect. With a view to study the effect that a modification of the group at this position has on the linear and nonlinear optical properties of the present compounds, we decided to acylate the amino group of **2b**, chosen as a model compound. To our surprise, the attempted diacylation of **2b** under standard conditions (excess ClCO$_2$Et/pyridine)[3–5] led to puzzling results, but, after some experimentation, we could successfully prepare carbamate **6** (Scheme 3).[36]

The much decreased electron-donating ability of the nitrogen atom of the carbamate group when compared to that of the free amino substituent gives rise to a very marked bathochromic shift ($\lambda_{max} = 685$ nm in DMSO) and to an increase of the second-order NLO response ($\mu\beta = 1050 \times 10^{-48}$ esu, $\mu\beta_0 = 442 \times 10^{-48}$ esu).

In conclusion, we have prepared a series of push–pull polyenes incorporating a 1,3-dithiole donor unit and a malononitrile dimer acceptor. The stereochemistry of these merocyanines has been fully established, and their push–pull character has been ascertained both experimentally and theoretically. The effect of the amino group on the linear (hypsochromic shift) and nonlinear (moderate $\mu\beta_0$ values) optical properties of the target compounds is explained by its electron-donating character, which can be tuned through carbamate derivatization. The second-order NLO response of 1,3-dithiole-derived merocyanines bearing either 2-amino-1,3,3-tricyanopropenylidene or dicyanomethylene groups is similar.

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Scheme 3.

19. General procedure for **2a,b**: To a stirred solution of the corresponding aldehyde **3a,b** (0.51 mmol) and 2-amino-1,1,3-tricyanopropene (**1**) (0.76 mmol) in 10 mL of absolute ethanol was added one drop of piperidine/ethanol (1:1). The mixture was refluxed under argon with exclusion of light for 2.5–5 h (TLC monitoring). After cooling, the resulting solid was isolated by filtration, washed with cold ethanol and pentane and dried. Compound **2a**: Purple solid (80 mg; 55%). Compound **2b**: Violet solid (80 mg; 51%).

20. Analytical data. For **2a**: mp: 254–256 °C; IR (Nujol, cm^{-1}): 3425, 3295 (N–H), 2211 (CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 2.14 (s, 3H), 2.16 (s, 3H), 6.67 (d, $J = 12.6$ Hz, 1H), 7.67 (d, $J = 12.6$ Hz, 1H), 8.43 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 12.9, 13.2, 46.7, 89.6, 106.0, 115.3, 116.2, 116.3, 127.5, 127.6, 147.2, 164.9, 167.1; HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{13}H_{11}N_4S_2$, 287.0420; found, 287.0395. For **2b**: mp: 262–263 °C; IR (Nujol, cm^{-1}): 3334, 3226 (N–H), 2210 (CN); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 2.06 (s, 3H), 2.08 (s, 3H), 6.35 (dd, $J = 12.4$ Hz, $J' = 13.1$ Hz, 1H), 6.69 (d, $J = 11.9$ Hz, 1H), 7.13 (dd, $J = 11.9$ Hz, $J' = 13.1$ Hz, 1H), 7.80 (d, $J = 12.4$ Hz, 1H), 8.55 (br s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 13.4, 13.8, 40.1, 95.9, 111.6, 115.5, 116.4, 116.8, 120.0, 128.0, 128.1, 145.7, 155.2, 155.6, 165.5; HRMS (ESI): [M+H]$^+$ m/z calcd for $C_{15}H_{13}N_4S_2$, 313.0576; found, 313.0573.

21. To a solution of *N,N*-dimethyl 2-(4,5-dimethyl-1,3-dithiol-2-yliden)ethylideniminium tetrafluoroborate (**4**) (0.34 mmol) in anhydrous DMF (3.6 mL), 2-amino-1,1,3-tricyanopropene (**1**) (0.38 mmol) and piperidinium acetate (0.38 mmol) were added. The mixture was stirred under argon for 6 hours at room temperature. Then, AcOEt (100 mL) was added and the resultant organic layer was washed with water (5 × 30 mL), dried (MgSO$_4$) and evaporated. The residue was purified by column chromatography (silica gel) using CH$_2$Cl$_2$ and then CH$_2$Cl$_2$/AcOEt (1:1). 65 mg (67%) of a purple solid was obtained, and identified as compound **2a**.

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23. Compound **2c** was prepared analogously to **2a,b**, but using **3c** as starting material. The resulting solid was purified by semipreparative HPLC (Waters Xbridge-C18 column, mobile phase: acetonitrile/water, 70:30, v/v), obtaining 71 mg (41%) of **2c**, as a dark blue solid. Analytical data for **2c**: mp: 199–200 °C; IR (Nujol, cm^{-1}): 3331, 3314 (N–H), 2212 (CN); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.00 (s, 3H), 2.03 (s, 3H), 6.37 (dd, $J = 11.7$ Hz, $J' = 14.0$ Hz, 1H), 6.43 (d, $J = 11.7$ Hz, 1H), 6.55 (dd, $J = 11.9$ Hz, $J' = 14.0$ Hz, 1H), 6.70 (dd, $J = 11.7$ Hz, $J' = 14.0$ Hz, 1H), 7.23 (dd, $J = 11.7$ Hz, $J' = 14.0$ Hz, 1H), 7.69 (d, $J = 11.7$ Hz, 1H), 8.68 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 °C) δ (ppm): 12.3, 12.6, 48.7, 97.7, 111.2, 113.9, 114.5, 115.0, 122.9, 123.2 (C4 and C5 of the dithiole ring), 125.3, 138.6, 146.6, 150.0, 153.2, 164.2; HRMS (ESI): [M+H]$^+$ m/z calcd for $C_{17}H_{15}N_4S_2$, 339.0732; found, 339.0716.

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36. To a stirred suspension of **2b** (0.43 mmol) in anhydrous CH$_2$Cl$_2$ was added (0 °C, argon atmosphere) triethylamine (8.7 mmol), and then, dropwise ethyl chloroformate (7.06 mmol) (*Caution*: very exothermic reaction!). The mixture was stirred for 5 min at 0 °C, and then for 2 h at room temperature. H$_2$O/CH$_2$Cl$_2$ 1:1 (20 mL) was then added, and the resulting solution was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic layer was dried (MgSO$_4$), evaporated and the residue purified by column chromatography (silica gel, CH$_2$Cl$_2$, then CH$_2$Cl$_2$/AcOEt (9:1) and finally CH$_2$Cl$_2$/AcOEt (6:4)). Compound **6** was isolated as a dark blue solid (107 mg; 65%). Analytical data for **6**: mp: >300 °C; IR (Nujol, cm^{-1}): 3225 (N–H), 2222 (CN), 1760 (O–CO–NH); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.26 (t, $J = 7.1$ Hz, 3H), 2.17 (6H, s), 4.19 (q, $J = 7.1$ Hz, 2H), 6.40 (t, $J = 12.7$ Hz, 1H), 6.90 (d, $J = 12.5$ Hz, 1H), 7.48 (t, $J = 12.7$ Hz, 1H), 7.95 (d, $J = 12.3$ Hz, 1H), 10.67 (br s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 13.1, 14.1, 62.2, 63.1, 93.3, 112.5, 114.4, 114.5, 115.2, 119.7, 128.7, 148.3, 152.0, 156.1, 159.2, 164.4; HRMS (ESI): [M+H]$^+$ m/z calcd for $C_{18}H_{17}N_4O_2S_2$, 385.0787; found, 385.0780.