



New class of hyperpolarizable push–pull organic chromophores by applying a novel and convenient synthetic strategy



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ABSTRACT

A new class of push–pull chromophore with an azomethine unit at a key position of the chromophore in order to increase the hyperpolarizability is reported. Additionally, a novel and convenient synthesis method is introduced which is particularly advantageous compared with known procedures because it offers high atom economy, the use of low cost reagents, and mild reaction conditions together with a reduced number of reaction steps.

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1. Introduction

Over the past two decades the rising demand for telecommunication services and high speed data transmission technologies has been the driving force for intense research on electro optic (EO) materials. Among all EO materials a new family of EO chromophores – conjugated organic molecules that are used to manipulate light by an electric field – is pointing the way to a revolution in telecommunications and information processing [1]. Organic non-linear optical chromophores generally have one electron-withdrawing group at one end and one electron-donating group at the other, linked together by extended conjugation.

To design and synthesize organic EO (OEO) materials Seth Marder's group [2] introduced a unified description of linear and nonlinear polarizability by showing correlation of the polarizabilities with a π -bond order alternation in a linear polymethine dye system. The introduction of furan-thiophene chromophore (FTC) and ring-locked, phenyltetraene-based chromophore (CLD) by Larry Dalton's group [3] turned out to be one of the major advances in OEO materials during the last few years. Larry Dalton's group also

explored the properties of conjugated organic systems, e.g., high NLO susceptibility [4], low dielectric constants [5], possibilities of structural modification [1], and ease of processability [6] which suited the FTC and CLD type chromophores for their applications in photonic devices [1,4–6]. Moreover, other researches in the field of OEO materials have been directed towards optimization of the material parameters at the molecular level. This includes shape and electronic optimization. Shape optimization has been performed not only in linear chromophores (e.g., using a conformationally locked polyene bridge for reduced dipolar interaction) but also on various other types of chromophores, such as spherical shape [7], X-shape [8] U-shape [9], H-shape [10] and Y-shape [11]. In parallel to the shape optimization, electronic optimization has also been examined by many research groups [12]. So far, the conventional synthetic strategy for preparing all type of push–pull organic non-linear optical chromophores has been to build the chromophore step by step from the electron-donating group towards the electron-withdrawing group. This synthetic scheme generally involves four steps. In the case of tertiary aromatic amines containing hydroxyl groups the protection of the hydroxyl groups is the first step. The second step involves Wittig reaction of donating groups bearing aldehyde with phosphonium salt containing a π -bridge. The third step, formylation of the bridge is performed through either Vilsmeier formylation using DMF/POCl₃ or by lithiation with, e.g., n-

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butyllithium followed by treatment with DMF. In the final step the chromophore is obtained via the Knoevenagel condensation reaction of the prepared intermediates with acceptor groups, e.g., tri-cyanofuran acceptor (TCF) in basic condition. As an example the synthesis of the benchmark chromophore FTC is shown in Scheme 1.

Hundreds of push–pull non-linear optical chromophores have been prepared using this conventional synthetic strategy with its numerous steps, leading to lower overall yields and higher overall costs. Hence the synthesis of the chromophores with high-yield, cost-effective chemical pathways as well as operational stability is still a challenge. In this communication we report a novel class of chromophores and its facile synthesis strategy.

2. Experimental

2.1. Materials and general methods

The precursors were purchased from Sigma Aldrich and ACROS used without further purification. All solvents were degassed according to standard techniques before use. ^1H and ^{13}C and NMR spectra were recorded on a Bruker Spectrospin Avance 400 device using dimethylsulfoxide- d_6 (DMSO- d_6) or CDCl_3 as solvent. The chemical shifts are given in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constant in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br.). The high resolution mass spectrum (HRMS) was measured on a Waters GTC Premier. The MS spectra were obtained using MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on a BIFLEXIII (Bruker Inc.) CHN-Elemental analyses were performed with a Perkin–Elmer Elemental Analyzer EA 2400 CHN. Thermogravimetric and differential thermogravimetric (TG-DTG) analyses were carried out on a SETRAM Setsys 16/MS instrument using an alumina pan in flow of Nitrogen from room temperature to $550\text{ }^\circ\text{C}$ with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. UV–Vis UV/vis absorption spectra were recorded using a Thermo Fisher Evolution 220 spectrophotometer.

2.2. Experimental details including characterization data

2.2.1. Synthesis of acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF)

Acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) was synthesized according to a method published in the literature [13] with slight modification. In a 100 mL round-bottomed flask, a solution of sodium ethoxide was prepared by adding sodium (0.09 g, 3.91 mmol) to ethanol (60 mL). To this solution 3-hydroxy-3-methyl-2-butanone (3.32 mL, 30 mmol) and malononitrile (4.00 g, 60 mmol) were added. The resulting mixture

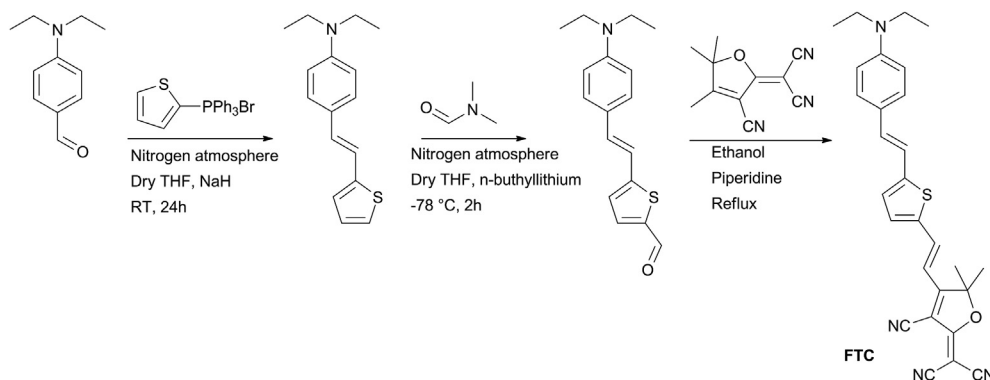
refluxed overnight. After concentration in vacuo, the residue was washed with diluted aqueous HCl. The crude precipitate was filtered and recrystallized from ethanol and gave the desired product, yield: 314 g (95%, yellow solid). 2.37 g (78%). $\text{C}_{11}\text{H}_9\text{N}_3\text{O}$ (199.209): calcd. C 66.32, H 4.55, N 21.09; found C 65.96, H 4.54, N 20.95. ^1H NMR (CDCl_3 , 400.1 MHz, $20\text{ }^\circ\text{C}$): δ = 1.63 (s, 6H), 2.36 (s, 3H), ppm. ^{13}C NMR (CDCl_3 , 100.62 MHz, $20\text{ }^\circ\text{C}$): δ = 14.30, 24.49, 58.65, 99.84, 104.94, 109.06, 110.48, 111.12, 175.28, 182.61 ppm.

2.2.2. Synthesis of key intermediate (KI) (E)-2-(3-cyano-4-(2-(5-formylthiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene) malononitrile

NaOH (0.009 g, 0.225 mmol) were added to a solution of 2,5-Thiophenedicarboxaldehyde (1.32 g, 9.32 mmol) and 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) (1.83 g, 9.19 mmol) in mixture of dry ethanol (60 mL) and dichloromethane (10 mL). The reaction mixture was refluxed for 6 h and the product precipitated during the reaction which was filtrated and washed with diethyl ether and dried in vacuum, yield: 2.51 g (85%, green solid) and it used without any purification in the next step. ^1H NMR (CDCl_3 , 400.13 MHz, $20\text{ }^\circ\text{C}$): δ = 1.78 (s, 6H, H-9), 6.87 (d, J = 16.2 Hz, 1H, H-10), 7.54 (d, J = 4.0 Hz, 1H, H-12), 7.79 (d, J = 4.0 Hz, 1H, H-13), 7.85 (d, J = 16.2 Hz, 1H, H-17), 9.98 (s, 1H, H-15) ppm. ^{13}C NMR (CDCl_3 , 100.61 MHz, $20\text{ }^\circ\text{C}$): δ = 25.38, 26.36, 97.85, 99.12, 101.19, 117.11, 133.20, 133.66, 136.44, 136.53, 137.95, 146.83, 147.34, 171.96, 182.62, 182.85 ppm. HRMS-EI: m/z calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$: 321.0572 $[\text{M}]^+$; found: 321.0567.

2.2.3. Synthesis of the chromophore 2-(3-cyano-4-((E)-2-(5-((E)-((4-(diethylamino)phenyl)imino)methyl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (BL)

A mixture of key intermediate (0.5 g, 1.56 mmol), *N,N*-diethyl-*p*-phenylenediamine (0.29 g, 1.71 mmol) and Na_2SO_4 (1.5 g, 1.71 mmol) was stirred for 24 h at room temperature in CH_2Cl_2 (10 mL) whereby its color changed to green. It was then concentrated and the product was precipitated by adding pentane (10 mL). The product was collected by filtration, washed with pentane twice and dried in vacuo as a green solid (0.62 g, 85%). $\text{C}_{27}\text{H}_{25}\text{N}_5\text{OS}$ (467.59): calcd. C, 69.35; H, 5.39; N, 14.98, S, 6.86; found C, 69.57; H, 5.42; N, 15.03; S, 6.90. ^1H NMR (CDCl_3 , 400.13 MHz, $20\text{ }^\circ\text{C}$): δ = 1.20 (t, J = 7.1 Hz, 6H, H-21), 1.74 (s, 6H, H-9), 3.41 (m, 4H, H-20), 6.65–6.73 (m, 3H, H10, H18), 7.32 (d, J = 9.1 Hz, 2H, H-17), 7.37 (d, J = 4.0 Hz, 1H, H-12), 7.44 (d, J = 4.0 Hz, 1H, H-13), 7.88 (d, J = 15.9 Hz, 1H, H-7), 8.62 (s, 1H, H-15) ppm. ^{13}C NMR (CDCl_3 , 100.61 MHz, $20\text{ }^\circ\text{C}$): δ = 12.81, 26.42, 44.75, 97.53, 97.93, 110.83, 111.21, 111.89, 112.00, 114.05, 123.83, 130.82, 136.04, 137.69, 139.52, 141.59, 144.18, 148.15, 151.80, 172.81, 175.62 ppm. MS (MALDI-TOF): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{N}_5\text{OS}$: 467.18 $[\text{M}+\text{H}]^+$; found: 468.0.



Scheme 1. Synthesis of the chromophore FTC.

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