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Dicarboxy-telechelic cooligomers with sequence structure tunable light absorption

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ABSTRACT

Alternating cooligomers of 5 pyrrole (P) and thiophene (T) units with a PTPTP sequence and carboxylic telechelic groups in α,α′-position are supposed to provide a low band gap and might be incorporated into degradable polymers. In this study we explored whether such new α,α′-ester linked π-conjugated alternating electron rich PTPTP cooligomers of defined size could be created following a Stille coupling synthesis pathway. The obtained cooligomers displayed in the absorption spectra λ_{max} between 341 and 379 nm in solution and between 346 and 410 nm in the solid state, which could be tuned by the substitution with donor type alkyl and alkoxy functions. A strong red shift of the absorption bands into the IR region of the spectrum with absorption maxima between 550 and 650 nm and further to 850 and 1000 nm could be obtained when additional charges by deprotonation or oxidation were introduced. The prepared semi conducting materials could be applied potentially as dyes for photoacoustic imaging or in sensors for oxidation monitoring.

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1. Introduction

Oligothiophenes are known for their good biocompatibility [1] and provide an emission spectrum, which is adjustable by the control of the energy level of the band gap. This makes oligothiophenes attractive candidates for organic dyes. The band gap and in this way the absorption range of thiophenes can be controlled by the parameters: conjugation length [2–4], mean deviation from planarity, aromatic resonance energy, and inductive or mesomeric electronic effects of substituents [5]. One approach for lowering the electronic band gap of thiophenes is the incorporation of highly electron-rich moieties, e.g. by coupling (oligo)thiophenes with 3,4-ethylenedioxypyrrole (EDOP) [6–8]. This effect can be enhanced by multiple alterations of electron poor and rich moieties [9]. In contrast to the diversity of oligothiophene bearing architectures [10,11] less is known about such cooligomers with alternating pyrrole (P) and thiophene (T) units. Only a few unsubstituted cooligomers providing a TPT or TPTPT architecture were prepared [4,9,12–15].

If such thiophene-based dyes would feature terminal reactive groups they could be covalently integrated into a polymer matrix. Here carboxyl groups seem to be most attractive because of their high reactivity and versatility of potential reaction partners. Although a huge variety of α,α′-linked carboxyl substituted oligothiopenes have been described [16–20] even less is known about α,α′-linked carboxyl substituted pyrrole–thiophene cooligomers. Only few examples of short α,α′-linked carboxyl substituted pyrrole–thiophene cooligomers are reported. α,α′-linked carboxyl substituted pyrrole–thiophene cooligomers of three units were prepared by Suzuki–Miyaura cross coupling [21], *via* Pd-mediated decarboxylative cross coupling [22], or by a cyclization strategy of 1,4-diketones [23]. However, the approach of cyclization of 1,4-diketones is limited when substituted cooligomers with thiophene and pyrrole units should be prepared. Here the palladium-catalyzed Stille coupling of organotin moieties with electrophiles such as aromatic halides has doubtless advantages because of their high tolerance of various substitution patterns [24–26].

In this context we explored whether well-defined oligothiophenes with terminal carboxyl groups could be prepared. Such well-defined oligomers can serve as model compounds for the corresponding polymers [27,28]. For the synthesis of the PTPTP cooligomers we selected a TPT core unit **15** (Scheme 2), to which differently substituted pyrrole derivatives bearing electron donating groups were attached to vary the electronic properties of the oligomers. The pyrrole substituents were supposed to lower the band gap in the resulting conjugated system and their electronic properties were controlled by the substituents, which were varied between ethyl groups, ethyl ether groups, and a bridged ethyl ether group. 3,4-substitued iodopyrrole monomers **6**, **10** and **12** containing ester side chains were selected as starting materials for the synthesis of alternating thiophene pyrrole cooligomers (Scheme 1) [21]. Ester side chains were selected as they are known to stabilize the pyrrole nucleus against oxidative degradation [29]. Iodo-substituted pyrroles, which are widely used as substrates in the Pd-catalyzed Stille coupling, were applied as starting materials because of their easy availability and their advantageous reactivity. First the synthesis of the pyrrole derivatives is presented, then the coupling reaction with the core unit is shown, and finally the

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tuning of the light absorption and photoluminescence properties of the obtained cooligomers are reported and discussed.

2. Experimental

2.1. Materials

Dimethyl 3,4-dihydroxy-1*H*-pyrrole-2,5-dicarboxylate **7** was obtained from Alfa Aesar (Karlsruhe, Germany). All other starting materials and solvents were purchased from Merck (Darmstadt, Germany) or Sigma Aldrich (Taufkirchen, Germany) and were of at least p.a. quality and used as received. Dry solvents were stored over molecular sieves under argon. Tetramethylethylendiamine (TMEDA) was stored over NaOH pellets and freshly distilled prior usage. Column chromatography was carried out with 230–400 mesh silica gel from Sigma Aldrich (Taufkirchen, Germany).

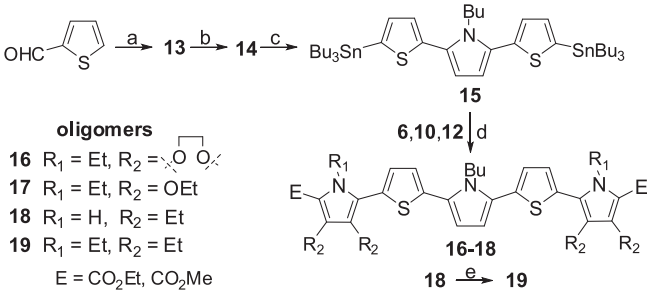
2.2. Physicochemical characterization methods

NMR spectra were recorded on a Bruker 500 MHz spectrometer (Bruker, Karlsruhe, Germany) at 500 and 100 MHz respectively for ^{1}H and ^{13}C NMR spectra, at 25 °C using the signal of the residual protonated solvent as internal standard (^{1}H: δ($CHCl_3$) = 7.26 ppm, δ(DMSO) = 2.49, δ(CH_3CN) = 1.94 ppm, δ(MeOH) = 3.31 ppm, δ(acetone-d^6) = 2.05 ppm and ^{13}C: δ($CDCl_3$) = 77.0 ppm, δ(DMSO) = 39.7 ppm, δ(acetone d^6) = 30.83, δ(MeOH-d^4) = 49.05 ppm). ^{13}C NMR-spectra were recorded with broadband ^{1}H-decoupling. High resolution Mass spectrometry was performed using a ESI-FTICRMS (Ionspec QFT-7, Varian Inc., Lake Forest, CA) equipped with a 7 T superconducting magnet and a Micromass Z-Spray ESI-Source (Waters Co., Saint-Quentin, France). Elementary analyses were performed on a FlashEA 1112 CHNS/O Automatic Elemental Analyser (Thermo Scientific, Karlsruhe, Germany). Fourier transform IR spectra were recorded on a Magna IR 550 series II (Thermo Nicolet, Waltham, USA) with a single beam diamond attenuated total reflection (ATR) unit. Melting transitions were determined on a melting point apparatus SMP3 (BIBBY Stuart, Staffordshire, UK). UV/visible absorption spectra were recorded in solvents of spectroscopic grade using quartz glass cuvettes of 1 cm path length on a Cary 50 Bio spectrophotometer (Varian Inc./Agilent Technologies, Santa Clara, USA) at 25 °C. Fluorescence emission spectra were measured using a LS50B Luminescence Spectrometer (Perkin Elmer, Mörfelden-Walldorf, Germany) at 25 °C. Samples were not degassed since in a reference experiment degassing did neither alter absorption nor fluorescence spectra in any detectable way. The samples were excited at absorption maxima, slit widths were set to 3 nm bandpass for excitation as well as for emission. Fluorescence spectra were corrected for variations in photomultiplier response over wavelength using correction curves generated on the instrument, followed by normalization considering the optical density of the sample at the excitation wavelength (OD(λ_{exc}) ⩽ 0.1).

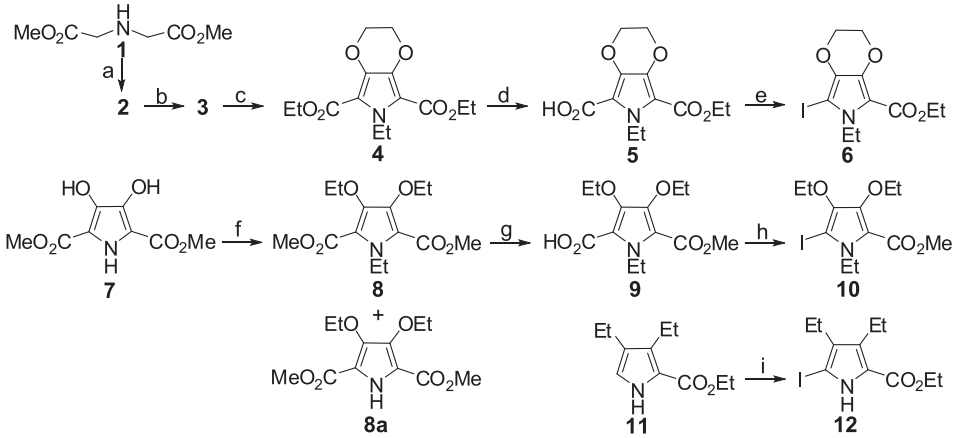
2.3. Syntheses and physico-chemical characterizations

2.3.1. 2-Ethyl N-ethyl-3,4-ethylenedioxypyrrole-2-carboxylate-5-carboxylic acid 5

To a solution of KO^{t}Bu (0.79 g, 2 eq, 6.9 mmol) in dry tetrahydrofurane (5 mL) were added 62 μL water (1 eq, 3.4 mmol) and stirred for 15 min at 0 °C. The suspension was added under intensive stirring to a solution of diethyl *N*-ethyl-3,4-ethylenedioxypyrrole-2,5-dicarboxylate **4** (1.03 g, 3.4 mmol) in 10 mL dry tetrahydrofurane at 0 °C. The orange brown suspension was stirred at room temperature for 16 h, diluted with 70 mL ice water and the obtained clear solution was extracted with 20 mL diethylether for impurity removal. After the aqueous phase was adjusted to pH 2–3 with $KHSO_4$ the orange turbid mixture was extracted with ethyl acetate (4 × 30 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The orange brown crude product was purified by column chromatography (ethyl acetate, R_f: 0.1) to yield 0.81 g (87%) of the product as a yellowish solid. A small amount of the product was further purified for analysis by recrystallization from heptane/ethanol to give 2-ethyl *N*-ethyl-



Scheme 2. Synthesis of oligomers 15–19, conditions: (a) divinylsulfone, 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride, NaAc, EtOH, 78 °C/12 h, 48%; (b) butyl amine, propionic acid, benzene, reflux/2 d, 75%; (c) *n*BuLi (1.25 eq), TMEDA, THF, (1.25 eq) Bu_3SnCl, −78 °C – rt; (d) $Pd(PPh_3)_4$, toluene, reflux/4 d, 52–60%; and (e) NaH, ethyl iodide, DMF, rt – 50 °C/4 h, 78%.0



Scheme 1. Synthesis of monomers 6, 10, 12, conditions: (a) diethylsulfate, 3 h, 100 °C, 61%; (b) diethyl oxalate, NaOEt/EtOH, 16 h, 78 °C, 54%; (c) dibromo ethane, K_2CO_3, DMF, 16 h, 120 °C, 55%; (d) 2 eq KO^{t}Bu, 1 eq H_2O, THF, 16 h, 0 °C – rt, 87%; (e) KI/I_2, $KHCO_3$, H_2O, 20 min, 50 °C, 98%; (f) diethylsulfate, K_2CO_3, acetone, 60 h, 60 °C, 38%; (g) 2 eq KO^{t}Bu, 1 eq H_2O, THF, 16 h/0 °C – rt, 72%; (h) KI/I_2, $KHCO_3$, H_2O, 25 min, 50 °C, 75%; and (i) 1,2-dichloroethane, KI/I_2, $KHCO_3$, H_2O, 2 h, 80 °C, 79%.

3,4-ethylenedioxypyrrole-2-carboxylate-5-carboxylic acid **5** as a colorless solid: mp. 189–190 °C; ^{1}H NMR (500 MHz, acetone-d^6, 25 °C): δ 4.72 (*q*, *J* = 7 Hz, 2H, N—*CH*$_2$), 4.30–4.25 (*m*, 6H, O—*CH*$_2$, O—*CH*$_2$*CH*$_2$—O), 1.31 (*t*, 3H, *J* = 7 Hz, *CH*$_3$), 1.23 (*t*, 3H, *J* = 7 Hz, *CH*$_3$); ^{13}C NMR (125 MHz, acetone-d^6, 25 °C): δ 162.5, 161.9, 138.0, 137.9, 112.2, 112.1, 67.2, 67.2, 61.6, 42.1, 18.3, 15.7; HRMS (3.8 kV, 25 °C): *m/z* = 270.09675 (*calcd* 270.09722 for [$C_{12}H_{15}NO_6$ + H]$^+$), 371.21641 (*calcd* 371.21767 for [$C_{12}H_{15}NO_6$ + NEt_3H]$^+$); Anal. C: 53.75 H: 5.64 N: 5.20 (*calcd* for $C_{12}H_{15}NO_6$ C: 53.53 H: 5.62 N: 5.20); IR ν 1708 (C=O), 1646 (C=O) cm^{-1}.

2.3.2. 2-Ethyl N-ethyl-3,4-ethylenedioxy-5-iodopyrrole-2-carboxylate 6

2-Ethyl-*N*-ethyl-3,4-ethylenedioxypyrrole-2-carboxylate-5-carboxylic acid **5** (0.74 g, 2.75 mmol) was dissolved in a solution of $KHCO_3$ (4.00 g, 14.5 eq, 40.0 mmol) in 40 mL water. A solution of iodine (1.40 g, 2 eq, 5.5 mmol) and KI (4.20 g, 9.2 eq, 25.3 mmol) in 18 mL water was added under stirring within 5 min at 50 °C. Immediately precipitation of a gray green solid occurred. After stirring for additional 20 min the excess of iodine was reduced by addition of $KHSO_3$ at room temperature. The colorless solution was extracted with methylene chloride (3 × 20 mL), the combined organic phases dried over $MgSO_4$, the solvent evaporated and the crude product purified by column chromatography (methylene chloride, R_f: 0.22) to yield 0.95 g (98%) of 2-ethyl *N*-ethyl-3,4-ethylenedioxy-5-iodopyrrole-2-carboxylate **6** as a white solid: mp. 60.5–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 4.32 (*q*, *J* = 7 Hz, 4H, N—*CH*$_2$, O—*CH*$_2$), 4.30–4.28/4.25–4.24 (*m*, 4H, O—*CH*$_2$*CH*$_2$—O), 1.35 (*t*, 3H, *J* = 7 Hz, *CH*$_3$), 1.22 (*t*, 3H, *J* = 7 Hz, *CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 159.7, 137.8, 134.5, 109.1, 66.4, 65.7, 64.6, 59.9, 44.4, 16.2, 14.5; HRMS (3.8 kV, 25 °C): *m/z* = 453.12295 (*calcd* 453.12448 for [$C_{11}H_{14}INO_4$ + NEt_3H]$^+$); IR ν 1672 (C=O) cm^{-1}.

2.3.3. Dimethyl N-ethyl-3,4-diethoxypyrrole-2,5-dicarboxylate 8

Diethyl sulfate (6.53 g, 3.1 eq, 41.9 mmol) was added dropwise within 5 min to a suspension of dry K_2CO_3 (2.00 g, 14.5 mmol) and dimethyl 3,4-dihydroxy-1*H*-pyrrole-2,5-dicarboxylate **7** (3.00 g, 13.5 mmol) in 35 mL dry acetone under argon atmosphere. The reaction mixture was stirred at 60 °C for 60 h. Ice water (25 mL) was added after solvent removal at low pressure. The clear solution was acidified to pH 4 by slow addition of $KHSO_4$ and was then extracted with ethyl acetate (4 × 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (ethyl acetate, R_f: 0.66) to yield 1.53 g (38%) of dimethyl *N*-ethyl-3,4-diethoxypyrrole-2,5-dicarboxylate **8** as a slightly yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 4.65 (*q*, *J* = 7 Hz, 2H, N—*CH*$_2$), 4.11 (*q*, *J* = 7 Hz, 4H, O—*CH*$_2$), 3.86 (*s*, 6H, O*CH*$_3$), 1.32 (*t*, 6H, *J* = 7 Hz, OCH_2—*CH*$_3$), 1.30 (*t*, 3H, *J* = 7 Hz, NCH_2—*CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 160.8, 141.8, 115.7, 70.4, 51.5, 41.7, 16.8, 15.4; HRMS (3.8 kV, 25 °C): *m/z* = 322.1274 (*calcd* 322.1267 for [$C_{14}H_{21}NO_6$ + Na]$^+$), 621.2649 (*calcd* 621.2635 for [2 × $C_{14}H_{21}NO_6$ + Na]$^+$), 338.1022 (*calcd* 338.1006 for [$C_{14}H_{21}NO_6$ + K]$^+$); IR ν 1716 (C=O) cm^{-1}. Dimethyl 3,4-diethoxy-1*H*-pyrrole-2,5-dicarboxylate **8a** could be separated as a by product (ethyl acetate, R_f: 0.59): colorless crystals, 0.32 g (9%); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.92 (*bs*, 1H, NH), 4.16 (*q*, *J* = 7 Hz, 2H, O—*CH*$_2$), 3.88 (*s*, 6H, O*CH*$_3$), 1.35 (*t*, 6H, *J* = 7 Hz, OCH_2—*CH*$_3$).

2.3.4. 2-Methyl N-ethyl-3,4-diethoxypyrrole-2-carboxylate-5-carboxylic acid 9

To a solution of KO^{t}Bu (0.93 g, 2 eq, 8.1 mmol) in abs. tetrahydrofurane (7 mL) were added 73 μL water (1 eq, 4.1 mmol) and stirred for 15 min at 0 °C. The suspension was added under intensive stirring to a solution of dimethyl *N*-ethyl-3,4-diethoxypyrrole-2,5-dicarboxylate **8** (1.33 g, 4.1 mmol) in 12 mL dry tetrahydrofurane at 0 °C. The reddish suspension was stirred at room temperature for another 16 h, diluted with 80 mL ice water and the obtained clear solution was extracted with 25 mL diethylether for impurity removal. The aqueous phase was adjusted to pH 2–3 with $KHSO_4$, the orange turbid mixture extracted with ethyl acetate (3 × 30 mL), the combined organic phases dried over $MgSO_4$, and the solvent evaporated at a temperature below 35 °C. The reddish crude product was purified by column chromatography (ethyl acetate, R_f: 0.1) to yield 0.87 g (72%) of 2-methyl *N*-ethyl-3,4-diethoxypyrrole-2-carboxylate-5-carboxylic acid **9** as a slightly purple solid; ^{1}H NMR (500 MHz, methanol d^4, 298 K) **9**: δ 4.93 (*bs*, 1H, COOH), 4.65 (*q*, *J* = 7 Hz, 2H, N—*CH*$_2$), 4.09 (*q*, *J* = 7 Hz, 2H, O—*CH*$_2$), 4.03 (*q*, *J* = 7 Hz, 2H, O—*CH*$_2$), 3.84 (*s*, 3H, O*CH*$_3$), 1.32 (*t*, 3H, *J* = 7 Hz, O—CH_2*CH*$_3$), 1.27 (*t*, 3H, *J* = 7 Hz, N—CH_2*CH*$_3$); ^{13}C NMR (According to the observed degradation processes in the material only selected signals are shown) (125 MHz, methanol d^4, 298 K): δ 162.6, 162.1, 143.1, 143.0, 117.1, 116.8, 71.7, 71.6, 52.0, 42.5, 28.7, 17.3, 15.8; HRMS (3.8 kV, 298 K): *m/z* = 308.1116 (*calcd* 308.1110 for [$C_{13}H_{19}NO_6$ + Na]; IR ν 1691 (C=O), 1651 (C=O) cm^{-1}.

2.3.5. Methyl N-ethyl-2-iodo-3,4-diethoxypyrrole-5-carboxylate 10

2-Methyl *N*-ethyl-3,4-diethoxy-pyrrole-2-carboxylate-5-carboxylic acid **9** (0.77 g, 2.6 mmol) was dissolved in a solution of $KHCO_3$ (3.75 g, 14.4 eq, 37.5 mmol) in 36 mL water. Within 5 min a solution of iodine (1.31 g, 2 eq, 5.1 mmol) and KI (3.95 g, 9.2 eq, 23.8 mmol) in 16 mL water was added under stirring at 50 °C. Immediately precipitation of a grayish solid occurred. After stirring for additional 20 min the excess of iodine was removed by addition of $KHSO_3$ at room temperature. The colorless solution was extracted with methylene chloride (3 × 20 mL), the combined organic phases dried over $MgSO_4$, the solvent evaporated, and the crude product purified by column chromatography (heptane/ethyl acetate 3:1 R_f: 0.38) to yield 0.71 g (75%) methyl *N*-ethyl-2-iodo-3,4-diethoxypyrrole-5-carboxylate **10** as a colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 4.35 (*q*, *J* = 7 Hz, 2H, N—*CH*$_2$), 4.08 (*q*, *J* = 7 Hz, 2H, O—*CH*$_2$), 4.03 (*q*, *J* = 7 Hz, 2H, O—*CH*$_2$), 3.83 (s, 3H, *OCH*$_3$), 1.34 (*t*, 6H, *J* = 7 Hz, OCH_2*CH*$_3$), 1.25 (*t*, 3H, *J* = 7 Hz, NCH_2*CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 160.4, 143.0, 140.2, 114.3, 75.2, 70.3, 70.1, 51.1, 45.6, 16.1, 15.6, 15.5; HRMS (3.8 kV, 298 K): *m/z* = 390.0206 (*calcd* 390.0178 for [$C_{12}H_{18}INO_4$ + Na]$^+$), *m/z* = 405.9945 (*calcd* 405.9918 for [$C_{12}H_{18}INO_4$ + K]$^+$), *m/z* = 757.0510 (*calcd* 757.0459 for [2 × $C_{12}H_{18}INO_4$ + Na]$^+$); IR ν 1680 (C=O) cm^{-1}.

2.3.6. N-Butyl-2,5-bis(5-(tributylstannyl)thiophen-2-yl)-pyrrole 15

n-butyllithium (7.2 mL, 2.5 eq, 11.5 mmol) was added at −78 °C dropwise via syringe to a solution of freshly distilled TMEDA (11 mmol, 1.28 g) and *N*-butyl-2,5-di(thiophen-2-yl)-pyrrole **14** (1.32 g, 4.59 mmol) in 30 mL dry THF. The reaction mixture was stirred at 0 °C for 30 min and then cooled again to −78 °C. A solution of tri-*n*-butyltin chloride (3.88 g, 2.6 eq, 11.9 mmol) in 11 mL dry tetrahydrofurane was added. The reaction mixture was stirred at −78 °C for an additional hour and subsequently over night at room temperature. The solution was diluted with heptane (100 mL) and poured in a mixture of ice/NH_4Cl and diethyl ether (100 mL). The organic layer was washed twice with saturated NH_4Cl and with brine, dried over $MgSO_4$, and the solvent removed in argon stream at room temperature and at low pressure. The obtained slightly yellow oily product **15** was used without further purification. ^{1}H NMR (500 MHz, acetone-d^6, 25 °C): δ 7.25 (*d*, 2H, *J* = 3.5 Hz, Th—*H*), 7.21 (*d*, 2H, *J* = 3.5 Hz, Th—*H*), 6.29 (*s*, 2H, Pyr—*H*), 4.24–4.21 (*m*, 2H, N—*CH*$_2$), 1.69–1.61 (*m*, 12H, *CH*$_2$), 1.55–1.49 (*m*, 2H, *CH*$_2$), 1.42–1.29 (*m*, 12H, *CH*$_2$), 1.25–1.11 (*m*, 14H, *CH*$_2$), 0.91(*t*, 18H, *J* = 7 Hz, *CH*$_3$), 0.76 (*t*, 3H, *J* = 7 Hz, *CH*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 142.6, 137.9, 137.8, 130.5, 128.6, 112.0, 46.5, 35.0,

31.0, 30.7, 29.1, 28.9, 21.3, 15.0, 14.9, 14.8, 12.4, 10.3; UV/vis (λ_{max}, $CHCl_3$): 330 nm.

2.4. General Stille coupling procedure

In a 25 mL round-bottomed flask *N*-butyl-2,5-bis(5-(tributylstannyl)thiophen-2-yl)pyrrole **15** and the monomers **6**, **10**, **12** (2.05 eq) respectively were dissolved in toluene (20 mL per mmol iodopyrrol), the mixture deaerated and an argon atmosphere was set up. Tetrakis (triphenylphosphine) palladium (0) (6 mol%) was added and the mixture heated under reflux for 4 days. The solvent was removed under low pressure and the crude product purified by column chromatography.

2.4.1. Diethyl 5,5′- (5,5′-(N-butyl-pyrrole-2,5-diyl)bis(thiophene-5,2-diyl)bis(N-ethyl-3,4-ethylenedioxypyrrole-2-carboxylate) 16

Stille-coupling of *N*-butyl-2,5-bis(5-(tributylstannyl)thiophen-2-yl)pyrrole **15** (0.65 g, 0.75 mmol) and 2-ethyl *N*-ethyl-3,4-ethylenedioxy-5-iodopyrrole-2-carboxylate **6** (0.52 g, 2.05 eq, 1.54 mmol). The yellow crude product was purified by column chromatography (ethyl acetate/hexane 1:1 R_f: 0.35) and recrystallized from heptane to yield 0.29 g (52%) **16** as a yellow solid: mp. 146–147 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.21 (*d*, *J* = 4 Hz, 2H, Th—*H*), 7.07 (*d*, *J* = 4 Hz, 2H, Th—*H*), 6.39 (*s*, 2H, Pyr—*H*), 4.46 (*q*, *J* = 7 Hz, 4H, N—CH_2CH_3), 4.36 (*q*, *J* = 7 Hz, 4H, O—CH_2), 4.36–4.34/4.28–4.26 (*m*, 8H, O—CH_2CH_2—O), 4.24–4.21 (*m*, 2H, N—$CH_2CH_2CH_2CH_3$), 1.65 (*pent*, *J* = 7.5 Hz, 2H, N—$CH_2CH_2CH_2CH_3$), 1.39 (*t*, 6H, *J* = 7 Hz, CH_3), 1.31 (*t*, 6H, *J* = 7 Hz, CH_3), 1.22 (*sex*, *J* = 7.5 Hz, 2H, N—$CH_2CH_2CH_2CH_3$), 0.82 (*t*, 3H, *J* = 7.5 Hz, N—$CH_2CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 160.6, 137.7, 135.8, 129.8, 129.1, 128.4, 128.1, 125.6, 116.1, 111.2, 105.3, 66.1, 65.4, 59.9, 45.2, 40.8, 33.4, 19.7, 16.9, 14.6, 13.6; HRMS (3.8 kV, 25 °C): *m/z* = 733.2453, 734.2484, 735.2505 (*calcd* 733.2468, 734.2517, 735.2501 for $[C_{38}H_{43}N_3O_8S_2]^+$), *m/z* = (*calcd* for $[C_{38}H_{43}N_3O_8S_2]^+$); Anal. C: 61.97 H: 5.85 N: 5.78 S: 8.65 (*calcd* for $C_{38}H_{43}N_3O_8S_2$ C: 62.19 H: 5.91 N: 5.73 S: 8.74); IR ν 1682 (C=O) cm^{-1}; UV/vis (λ_{max}, $CHCl_3$): 291 nm (log ε = 4.35), 379 nm (log ε = 4.62).

2.4.2. Dimethyl 5,5′- (5,5′-(N-butylpyrrole-2,5-diyl)bis(thiophene-5,2-diyl)bis(N-ethyl-3,4-diethoxypyrrole-2-carboxylate) 17

Stille-coupling of *N*-butyl-2,5-bis(5-(tributylstannyl)thiophen-2-yl)-1*H*-pyrrole **15** (0.44 g, 0.50 mmol) and methyl *N*-ethyl-2-iodo-3,4-diethoxypyrrole-5-carboxylate **10** (0.38 g, 2.05 eq, 1.0 mmol). The orange crude product was purified by column chromatography (ethyl acetate/hexane 1:4 R_f: 0.28) and recrystallized from heptane to yield 0.225 g (59%) **17** as a bright yellow solid: mp. 77–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.13 (*d*, *J* = 3.5 Hz, 2H, Th—*H*), 7.07 (*d*, *J* = 3.5 Hz, 2H, Th—*H*), 6.41 (*s*, 2H, Pyr—*H*), 4.39 (*q*, *J* = 7 Hz, 4H, N—CH_2CH_3), 4.26–4.23 (*m*, 2H, N—$CH_2CH_2CH_2CH_3$), 4.15 (*q*, *J* = 7 Hz, 4H, O—CH_2), 4.00 (*q*, *J* = 7 Hz, 4H, O—CH_2), 3.87 (s, 6H, OCH_3), 1.65–1.56 (*pent (br)*, *J* = 7.5 Hz, 2H, N—$CH_2CH_2CH_2CH_3$), 1.39 (*t*, 6H, *J* = 7 Hz, CH_3), 1.32 (*t*, 6H, *J* = 7 Hz, CH_3), 1.26 (*t*, 6H, *J* = 7 Hz, CH_3), 1.21 (*sex*, *J* = 7.5 Hz, 2H, N—$CH_2CH_2CH_2CH_3$), 0.79 (*t*, 3H, *J* = 7.5 Hz, N—$CH_2CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 161.2, 143.3, 136.3, 135.9, 129.5, 128.4, 125.6, 121.7, 111.1, 110.1, 70.2, 69.8, 51.0, 45.2, 41.1, 33.3, 19.7, 17.0, 15.6, 15.5, 13.6; HRMS (3.8 kV, 25 °C): *m/z* = 766.3205 (*calcd* 766.3196 for $[C_{40}H_{51}N_3O_4S_2 + H]^+$), *m/z* = 788.3033 (*calcd* 788.3015 for $[C_{40}H_{51}N_3O_4S_2 + Na]^+$), *m/z* = 1553.6178 (*calcd* 1553.6133 for [2 x $C_{40}H_{51}N_3O_4S_2 + Na]^+$), *m/z* = 804.2791 (*calcd* 804.2755 for $[C_{40}H_{51}N_3O_4S_2 + K]^+$); Anal. C: 62.48 H: 6.60 N: 5.49 S: 8.20 (*calcd* for $C_{40}H_{51}N_3O_4S_2$ C: 62.72 H: 6.71 N: 5.49 S: 8.37); IR ν 1689 (C=O) cm^{-1}; UV/vis (λ_{max}, $CHCl_3$): 364 nm (log ε = 4.54).

2.4.3. Diethyl 5,5′-(5,5′-(N-butyl-pyrrole-2,5-diyl)bis(thiophene-5,2-diyl)bis(3,4-diethylpyrrole-2-carboxylate) 18

Stille-coupling of *N*-butyl-2,5-bis(5-(tributylstannyl)thiophen-2-yl) pyrrole **15** (2.68 g, 3.1 mmol) and ethyl 3,4-diethyl-5-iodo-1*H*-pyrrole-2-carboxylate **12** (2.04 g, 2.05 eq, 6.4 mmol). Heptane (20 mL) was added to the orange/brown reaction mixture at room temperature. The precipitate was washed twice with heptane (20 mL) and the residue was further purified by column chromatography (methylene chloride, R_f: 0.14) to yield 1.13 g (54%) **18** as an orange solid: mp. 188 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.94 (*bs*, 2H, NH), 7.14 (*d*, *J* = 4 Hz, 2H, Th—*H*), 7.04 (*d*, *J* = 4 Hz, 2H, Th—*H*), 6.40 (*s*, 2H, Pyr—*H*), 4.36 (*q*, *J* = 7 Hz, 4H, OCH_2), 4.24–4.21 (*m*, 2H, N—CH_2), 2.79 (*q*, *J* = 7.5 Hz, 4H, Pyr—CH_2), 2.68 (*q*, *J* = 7.5 Hz, 4H, Pyr—CH_2), 1.67–1.60 (*m*, 2H, $NCH_2CH_2CH_2CH_3$), 1.38 (*t*, *J* = 7.5 Hz, 6H, $COOCH_2$—CH_3), 1.24–1.19 (*m*, 14H, $NCH_2CH_2CH_2CH_3$, Pyr—CH_2—CH_3), 0.82 (*t*, 3H, *J* = 7.5 Hz, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 161.4, 134.2, 134.1, 133.7, 128.4, 126.3, 126.0, 124.7, 124.1, 118.4, 111.1, 60.1, 45.2, 33.4, 19.7, 18.3, 17.7, 15.9, 15.8, 14.5, 13.6; HRMS (3.8 kV, 25 °C): *m/z* = 673.3025 (*calcd* 673.3003 for $[C_{38}H_{47}N_3O_4S_2]^+$); Anal. C: 67.37 H: 7.06 N: 6.34 S 9.49 (*calcd* for $C_{38}H_{47}N_3O_4S_2$ C: 67.72 H: 7.03 N: 6.24 S: 9.52); IR ν 3315 (NH), 1657 (C=O) cm^{-1}; UV/vis (λ_{max}, $CHCl_3$): 378 nm (log ε = 4.60), 303 nm (log ε = 4.24).

2.4.4. Diethyl 5,5′- (5,5′-(N-butylpyrrole-2,5-diyl)bis(thiophene-5,2-diyl)bis(N-ethyl-3,4-diethylpyrrole-2-carboxylate) 19

Sodium hydride (0.05 g, 10 eq, 2.2 mmol) was slowly added to a solution of diethyl 5,5′-(5,5′-(*N*-butylpyrrole-2,5-diyl)bis(thiophene-5,2-diyl)bis(3,4-diethylpyrrole-2-carboxylate) **18** (0.15 g, 0.22 mmol) in dry dimethyl formamide (5 mL) at 0 °C. After stirring for 15 min at 0 °C iodoethan (0.15 g, 4.2 eq, 0.93 mmol) was added to the orange/brown suspension via a syringe, the mixture was stirred at room temperature over night and finally 4 h at 50 °C to complete reaction. By pouring in saturated aqueous NH_4Cl at 0 °C the reaction was quenched, the solvent was removed at low pressure, and the obtained yellow crude product was purified by column chromatography (ethyl acetate/hexane 3:2 R_f: 0.45) to yield 0.13 g (78%) **19** as a pale yellow solid: mp. 59–60 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.09 (*d*, *J* = 3.5 Hz, 2H, Th—*H*), 7.00 (*d*, *J* = 3.5 Hz, 2H, Th—*H*), 6.42 (*s*, 2H, Pyr—*H*), 4.35 (*q*, *J* = 7 Hz, 4H, OCH_2), 4.29 (*q*, *J* = 7 Hz, 4H, N—CH_2CH_3), 4.26–4.23 (*m*, 2H, N—$CH_2CH_2CH_2CH_3$), 2.78 (*q*, *J* = 7.5 Hz, 4H, Pyr—CH_2), 2.42 (*q*, *J* = 7.5 Hz, 4H, Pyr—CH_2), 1.68–1.62 (*m*, 2H, N—$CH_2CH_2CH_2CH_3$), 1.40 (*t*, *J* = 7 Hz, 6H, $COOCH_2$—CH_3), 1.29 (*t*, 6H, *J* = 7 Hz, Pyr—CH_2—CH_3), 1.20 (*t*, 6H, *J* = 7.5 Hz, Pyr—CH_2—CH_3), 1.29–1.20 (*m*, 2H, N—$CH_2CH_2CH_2CH_3$), 1.06 (*t*, 6H, *J* = 7.5 Hz, N—CH_2CH_3), 0.81 (*t*, 3H, *J* = 7.5 Hz, N—$CH_2CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 161.7, 136.7, 133.8, 132.1, 129.7, 128.5, 128.3, 126.0, 125.7, 118.9, 110.9, 59.6, 45.1, 41.3, 33.4, 19.7, 19.2, 17.7, 17.4, 16.6, 16.1, 14.3, 13.5; HRMS (3.8 kV, 25 °C): *m/z* = 730.3701 (*calcd* 730.3712 for $[C_{42}H_{55}N_3O_4S_2 + H]^+$), *m/z* = 752.3530 (*calcd* 752.35317 for $[C_{42}H_{55}N_3O_4S_2 + Na]^+$); IR ν 1693 (C=O); UV/vis (λ_{max}, $CHCl_3$): 341 nm (log ε = 4.40), 285 nm (log ε = 4.35).

3. Results and discussion

The general synthetic route to the pyrrole monomers is illustrated in Scheme 1. Compound **12** is an already known pyrrole substrate that is frequently used in the porphyrinoid synthesis [30] and in the Suzuki cross coupling [21]. **12** could be easily obtained in good yield by iodination of the commercially available pyrrole ester **11**. The ether substituted new iodo monomers **6**, **10** were prepared according to procedures described in Refs. [49,50] and were isolated in 15.5% (5 steps) and 20.5% (3 steps) overall yield, respectively.

The 1-ethyl-3,4-dihydroxy-1H-pyrrole-2,5-dicarboxylic acid diethylester **3** was obtained by condensation of *N*-ethylated dimethyl iminodiacetate **2** [31] and diethyl oxalate and subsequent ring-closure under basic conditions [32]. The bis-*O*-alkylation of **3** with dibromo ethane resulted in the corresponding bridged 3,4-diether **4** [8]. Precursor **8** could be obtained in moderate yield in a one-step reaction by alkylation of the commercially available dihydroxypyrrolediester **7** using diethylsulfate in acetone [33]. It is noteworthy to mention that the bis-*O*-alkylated pyrrole **8a** could be isolated as a byproduct in 9% yield. In general, *N*-alkylation of the pyrrole nitrogen is expected to proceed faster [34]. The observed moderate yields for alkylation reactions of dihydroxypyrroles can be explained by the limited reactivity of the highly resonance stabilized intermediary formed dianions of **3** and **7** as well as by the possible formation of colored C2-alkylated products [34].

Subsequent treatment of **4** and **8** with potassium *tert*-butoxide/water resulted in mono hydrolsysis [35] and the new pyrrole (mono) carboxylic acids **5** and **9** were formed. In both cases the corresponding *bis* carboxylic acids were separated as by products in yields below 10% but were not further investigated. Unexpectedly, precursor **9** showed a tendency for decomposition. Slow decarboxylation at room temperature and cleavage of the second ester bond even at 4 °C within some weeks was observed. In contrast, compound **5** was more stable. Finally, the building blocks **6** and **10** could be successfully obtained in good yields by iododecarboxylation [36,37] of **5** and **9** in the presence of the remaining ester group.

The synthesis of the cooligomers **16**–**18** could be achieved by Pd-catalyzed Stille coupling reaction of the iodo monomers **6**, **10**, **12** with the tributylstannyl substituted precursor **15** that was prepared according to procedures (Scheme 2) described in Refs. [26,31,51,52]. The reaction of thiophene carbaldehyde with divinylsulfone resulted in 1,4-diketone **13** [38] and subsequent condensation with butylamine in the presence of propionic acid catalyst afforded *N*-butyl-2,5-bis(2-thienyl)-pyrrole **14** [13,14]. Compound **15** was prepared from **14** using an 10% excess of *n*BuLi and tributyltin chloride, to ensure complete distannylation [39]. The distannyl intermediate **15** could not be isolated in pure form since chromatography on silica resulted in destannylation. Therefore **15** was used without further purification in the Stille coupling protocol with the iodopyrrols **6**, **10**, **12** and the intensive yellow/orange oligomers **16**–**18** could be obtained in moderate yields of 52–59% when refluxed in toluene for 96 h [40]. Side reactions of the Stille coupling such as destannylation [41] and homocoupling of the stannyl compound [42] might have added to the observed moderate yields.

Cooligomer **19** could be obtained by *N*-alkylation of **18** with ethyl iodide in good yield when sodium hydride was used as base [43]. The cooligomers **16**–**19** of intensive yellow or orange color were obtained after purification by chromatography on silica and were stable at room temperature. Characteristic experimental data are summarized in Table 1. The compounds could also be validated by elemental analysis and high resolution mass spectroscopy.

The structures and substitution pattern of the cooligomers **16**–**19** were confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy in chloroform. The obtained proton spectra are presented in Fig. 1.

The symmetric cooligomers **16**–**19** show three aromatic signals: a typical singlet at around 6.40 ppm, which belongs to the central pyrrol unit (H^{a}), and two doublets at about 7.00–7.07 ppm and 7.09–7.21 ppm with coupling constants between 3.5 and 4.0 Hz, indicating the presence of two adjacent protons in the thiophene units ($H^{b/c}$). The typical broad NH – signal of unsubstituted pyrrol units in oligomer **18** was detected at around 9 ppm. Different substitution pattern did not significantly influence the position of the aromatic proton signals.

The IR spectra of the oligomers show an intense band between 1650 and 1690 cm^{-1} corresponding to the vibration band of the carbonyl group. **18**, which showed the lowest value of this vibration band, displayed additionally an intense band at 3315 cm^{-1} attributed to the vibration of the NH group.

Spectroscopic properties of the cooligomers **16**–**19** were measured from solution from chloroform and as thin film, which both were freshly prepared. UV/vis and Photoluminescence (PL) spectra of **16**–**19** are shown in Fig. 2 and characteristic data are summarized in Table 2.

The UV/vis absorption spectra of the cooligomers **16**–**19** in chloroform resulted in spectra, which are typical for molecularly dissolved mixed heteroaromatic oligomers: a strong absorption in the visible region at ~350–415 nm, which corresponds to the π–π^{*} – intra-chain transition [14,44]. The absorption maxima were located at 379, 378, 364, and at 341 nm for the compounds **16**, **18**, **17**, and **19** respectively. In addition, weaker vibronic bands could be determined for higher energies, which remained in measurements of the films in the solid state.

The main absorption of oligomer **16** at 379 nm was red shifted by 38 nm compared to **19**. Here, the appending ethylenedioxy bridges in **16** across the 3- and 4 positions of edge pyrrole units add electron density (by hyperconjugation and mesomeric effects) to the aromatic ring [6], causing a rise of the HOMO level of the conjugated π-system and in that way reduced the energy of the π–π^{*} transition, which resulted in a lowering of the electronic band gap [8]. The observed hypsochromic shift in the absorption of **17** of 15 nm compared to **16** can be explained by an increased steric impact of the OEt groups in the β,β'-position, causing a less effective π –π – conjugation in the oligomer. Interestingly, the cooligomers **16** and **18** exhibited nearly identical absorption curves although the electronic properties were different (**18** possesses less donor ability). Here, the steric interactions seemed to play a crucial role: cooligomer **18** contained only the central *N*-alkylated pyrrole unit therefore the aromatic backbone is more planar oriented compared to **16**, which enabled a more effective π–π – conjugation resulting in a decrease in the HOMO–LUMO gap. *N*-Alkylation of **18** induced a significant out-of plane twist in the aromatic backbone. As a result, the absorption of **19** showed a remarkable blue shift of 37 nm [13,45].

A broadening of the absorption could be observed in case of the cooligomers **16**, **17** and **19** in the solid state of casted films obtained by spin coating of methylene chloride solutions on quartz glass. The absorption spectra of the films displayed an onset wavelength at around 650 nm and λ_{max}s between 346 and 388 nm, which were compared to λ_{max}s obtained from solution between 5

Table 1
Properties and characteristic experimental data of oligomers **16**–**19**.

Compd.	Isolated yield (%)	Melting range (°C)	^{1}H-NMR δH^{a}, $H^{b,c}$ (ppm)	IR ν C=O, N–H (cm^{-1})
16	52[a]	146–147	6.39, 7.21, 7.07	1682
17	59[a]	77–78	6.41, 7.13, 7.07	1689
18	54[a]	188	6.40, 7.14, 7.04	1657, 3315
19	78[b]	59–60	6.42, 7.09, 7.00	1693

[a] By Stille coupling reaction.
[b] By alkylation reaction.

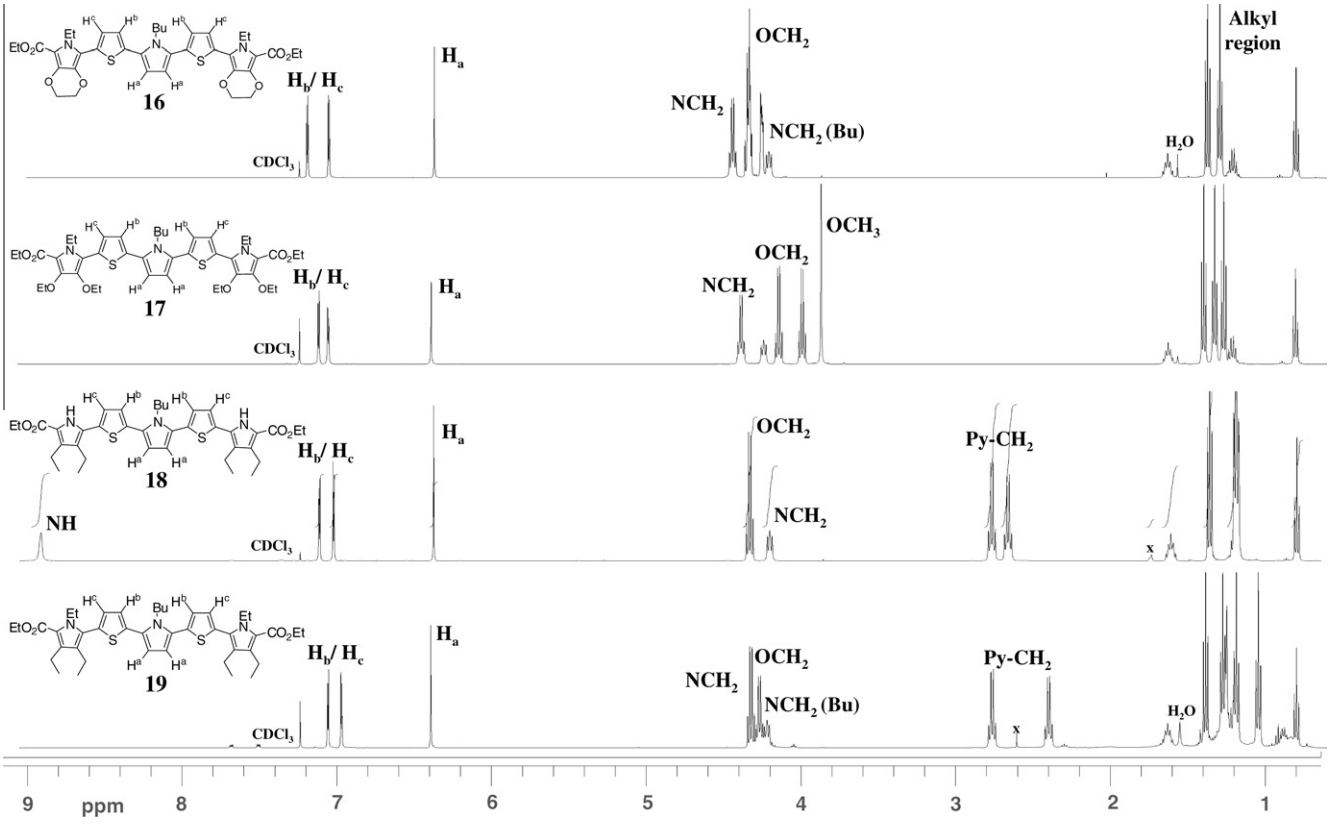


Fig. 1. 500 MHz ^{1}H-NMR spectra of oligomers **16**–**19** in $CDCl_3$.

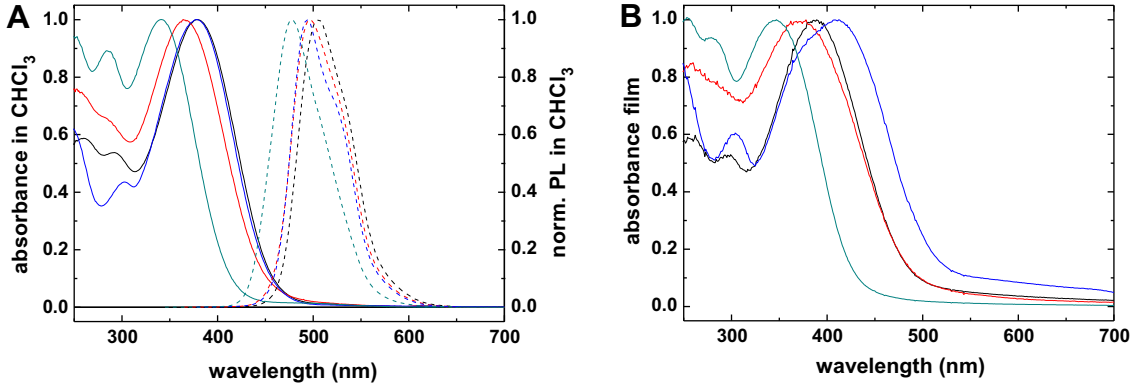


Fig. 2. Spectroscopic properties of cooligomers **16**–**19** in solution and as film, green: **19**, blue: **18**, red: **17**, and black: **16**. (A): UV/vis (solid line) and normalized PE – spectra (dashed line) in $CHCl_3$; (B): UV/vis thin film spin-cast from methylene chloride solutions.

Table 2
Electronic properties of cooligomers **16**–**19**: measurements in chloroform and solid state.

Compd.	Absorption λ_{max} (nm)/log ε	Band gap (eV)	Emission (PL) λ_{max} (nm)	Stokes shift (nm)	Absorption solid λ_{max} (nm)
16	291/4.35 379/4.62	2.7	506	127	296 388
17	364/4.54	2.8	496	132	371
18	303/4.24 378/4.60	2.7	494	116	304 410
	285/4.35	3.0	478	137	254
19	341/4.40				279 346

and 10 nm red-shifted, indicating a more aggregated configuration. A stronger red shift of λ_{max} of 34 nm and an onset wavelength >700 nm was observed for oligomer **18**, which can be attributed to a more orientated or more planar solid state arrangement and

stronger π–π interactions, because of the less sterically hindered molecular architecture.

In the photoemission (PE) spectra the cooligomers **16**, **17**, **18**, **19** emitted green or yellow green light at λ_{max} = 506, 496, 494 and 478 nm respectively. However, the vibronic fine structure was not well resolved and only a small shoulder, related to vibronic fingerprints. In case of the cooligomers **16**–**18** this shoulder was determined at wavelengths at about 530 nm. No significant differences could be observed in the emission intensities of the absorption corrected PL-spectra (Fig. 3). The slightly less intensive emission in case of **16** and **17** compared to the alkyl substituted cooligomers **18** and **19** was probably related to a certain quenching effect by the ether substituents.

The observed Stokes shifts were quite large between 116 nm for **18** and 137 nm in case of cooligomer **19**. A Stokes shift of 142 nm was reported for an alternating thiophene pyrrole pentamer with *N*-alkyl substitution in acetonitrile while the unsubstituted derivate showed a reduced Stoke shift of only 93 nm [45]. The differences in the Stokes shift between **18** and **19** were probably related to the different *N*-substitution, which strongly influenced the rigidity and the degree of freedom in both oligomers. In general, a closer geometric match between the ground and the excited-state causes smaller Stoke shifts [46].

The cooligomers **16**–**19** were soluble in most commonly used solvents, with some limitations: **18** was non-soluble in alkanes and poorly soluble in butanol, **16** was only poorly soluble in methanol, acetonitrile and DMSO. The absorption maxima of the cooligomers **16**–**19** in various solvents were summarized in Table 3.

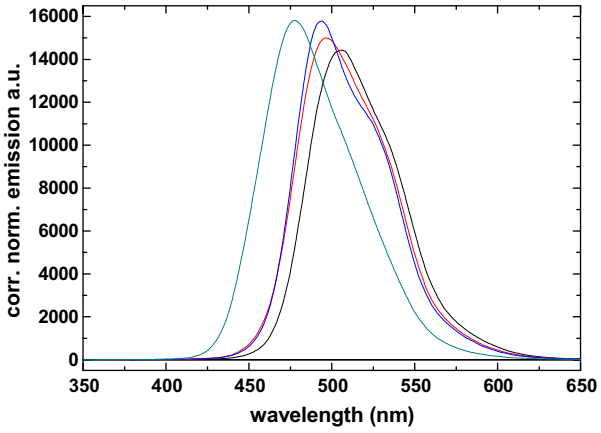


Fig. 3. Normalized photoemission-spectra of cooligomers **16**–**19** in $CHCl_3$ (OD 0.05–0.1) green: **19**, blue: **18** red: **17**, and black: **16**.

The change of solvent polarity did not result in remarkable changes in the absorption curves of the oligomers **16**–**19**, which would indicate molecular organization or aggregation. Only a slight red shift in range of 5–15 nm was observed in case of **16**–**18**, when the spectra in non-polar cyclohexane and polar dimethyl sulfoxide are compared. This can be explained by a stabilization of a more planar arrangement of the aromatic units in DMSO. In addition, intermolecular stacking did not seem to occur as no thermochromic changes in solution could be observed in exemplary measurements in heptane and chloroform solutions of **16** and **19** at different temperatures in range of 12–35 °C.

Finally, the tuning of the absorption by protonation and oxidation was explored. When acetic acid was used as a solvent for **16**–**18** an additional weak absorption band at longer wavelengths appeared, which indicated the formation of cationic species in low concentration. However, no significant changes of the absorption spectra in comparison to chloroform could be observed – protonation of the only weak basic pyrrole nitrogen atoms by acetic acid is not favoured. In contrast, when stronger acids such as dichloroacetic acid or trifluoroacetic acid were added to the cooligomers **16**–**19** intense color changes and an intensive red shift of λ_{max} occurred, indicating the formation of different cationic species [47,48]. When compound **17** was dissolved in acetic acid and trifluoroacetic acid was added (Fig. 4A), protonation of the first nitrogen resulted in a red shift of the absorption to λ_{max} around 650 nm. When protonation of the second nitrogen occurred, λ_{max} was further red shifted to around 950 nm. This color shift can be explained by a planarization of the formerly twisted backbone as the generated charges on the nitrogen atom of the molecule were stabilized by the conjugated system. A similar red-shift but to a much lower extent ($\Delta\lambda_{max}$ = 162) was observed when thiophene modified azulenes were treated with TFA and were attributed to the conjugation of the azulenium cation with the thiophene substituents [49].

Solutions of similar color could be retrieved by chemical oxidation of **16**–**19** with $FeCl_3$ in acetonitrile. The oxidation shifted absorption bands of the compounds to λ_{max} between 550 and 650 nm, as well as 800 and 1000 nm (Fig. 4B). This formation of radical cations, which are stabilized by conjugation, was accompanied by a strong red shift of the absorption in the NIR region and can be explained again by the more planar structure of the cations [50].

Table 3
Absorption maxima in different solvents (broad: main absorption).

Compd.	Hept. λ_{max} (nm)	Cyhex. λ_{max} (nm)	$CHCl_3$ λ_{max} (nm)	^{n}BuOH λ_{max} (nm)	CH_3CN λ_{max} (nm)	CH_3OH λ_{max} (nm)	DMSO λ_{max} (nm)	HAc λ_{max} (nm)
	248	284	260	261	261	260	264	259
16	**376**	**372**[b]	291	293	287	293	295	293
			379	**377**	**375**	**374**[b]	**386**	**380**
								679[c]
	252	253		254	254	253		**362**
17	**362**	**361**[b]	**364**	294	**359**	**357**	**370**	515[c]
				363				
			303	304	298	299	302	301
18	[a]	[a]	**378**	**377**[b]	**375**	**372**	**383**	**382**
								666[c]
	252	252		254	252	254		
19	278	280	285	284	281	285	281	285
	340	**339**[b]	**341**	**341**	**340**[b]	**338**[b]	**341**[b]	**341**

[a] Not soluble.
[b] Poorly soluble.
[c] Weak.

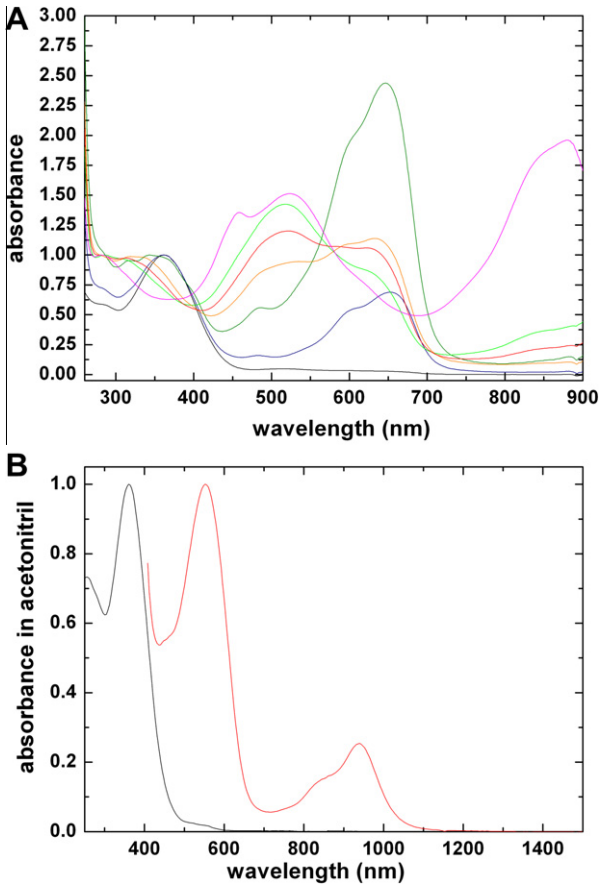


Fig. 4. (A) Not normalized absorption spectra of compound **17** after successive addition of trifluoroacetic acid (TFA) in acetic acid: black absorption of **17** in acetic acid, blue with 5 vol.% TFA, dark green with 20 vol.% TFA, light green with 70 vol.% TFA, orange with 80 vol.% TFA, red with 90 vol.% TFA, purple in 100 vol.% TFA and (B) Normalized absorption spectra of compound **17** after oxidation with $FeCl_3$ in acetonitrile, black **17** in CH_3CN, red **17** in acetonitrile oxidized with $FeCl_3$.

4. Conclusion

The synthesis of a class of alternating electron-rich and electron-poor pyrrole–thiophene cooligomers with telechelic ester functionalized rims (2 position) by a Stille coupling protocol was presented. In this context we described the synthesis of a family of electron rich 3,4-substituted mono iodo alkoxy pyrroles as monomers for the alternating pyrrole–thiophene cooligomers. The obtained cooligomers displayed in the absorption spectra λ_{max} between 341 and 379 nm in solution and between 346 and 410 nm in the solid state, which could be tuned by the substitution with donor type alkyl and alkoxy functions [6]. Furthermore, it could be shown that the adsorption properties of the alternating pyrrole–thiophene cooligomers were influenced by the steric interaction of the side chains and orientation and twisting of the aromatic backbone [13,45]. A strong red shift of the absorption bands into the IR region of the spectrum with absorption maxima between 550 and 650 nm and further to 850 and 1000 nm could be obtained when additional charges by deprotonation or oxidation were introduced. A red shift by protonation was also reported for other pyrrole bearing moieties as well but not to such an extent [51]. As the presented TPTPT cooligomers possess a high solubility and feature additional telechelic carboxyl groups, which enable further post-functionalization with e.g. a degradable matrix, they are interesting candidates for multifunctional polymers applied e.g. in nanoparticles for photoacoustic imaging or as sensors for oxidative degradation processes [52–55].

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