SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
20 (2014)

SYNTHESIS AND CHARACTERIZATION OF PUSH-PULL MOLECULES BEARING TETRAFLUOROBENZENE CENTRAL ACCEPTOR MODIFIED WITH TWO PERIPHERAL HEXYLOXY AND DIHEXYLAMINO DONORS

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Received March 31, 2014

Starting from 1,4-diiodotetrafluorobenzene or 1,4-bis(5-bromothiophene-2-yl)tetra-fluorobenzene, four new push-pull molecules were synthesized via twofold cross-coupling reactions. Suzuki-Miyaura and Sonogashira reactions were employed to gain access to target molecules. The central tetrafluorobenzene acceptor unit was modified by two peripheral N,N-dihexylamino and O-hexyloxy groups with different donating ability to generate quadrupolar D-π-A-π-D system with tailored intramolecular charge-transfer. The length, planarity and composition of the π-linker between the acceptor and donors was modified by combination of 1,4-phenylene, 2,5-thienylene and acetylenic subunits in order to finely tune the linear as well as nonlinear optical properties.

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Introduction

Fluorinated organic molecules are of current wide interest of organic chemists [1-3]. Due to its high electronegativity, fluorine atom represents an interesting option for π-conjugated system polarization and generation of the so-called push-pull system [4]. In such push-pull molecules, an intramolecular charge-transfer (ICT) from the electron donor to the electron acceptor takes place, and the molecule constitutes a D-π-A system [5]. Push-pull molecules possess plenty of interesting and useful properties such as distinct color, redox properties, dipolar character, thermal stability, supramolecular assemblies, etc. Hence, push-pull chromophores found wide applications in polymers, pharmacy or optoelectronic devices such as semiconductors, organic light-emitting diodes (OLEDs) and dye-sensitizing solar cells (DSSCs) [6-11]. In recent years, tetrafluorobenzene (TFB) has been utilized as well-accessible structural motive used for the construction of various push-pull or push-pull-push molecules [12-15]. Beside the aforementioned properties, these molecules showed also nonlinear optical (NLO) properties, mainly second- and third-order nonlinearities including two-photon absorption [16-20]. In our previous work focused on designing novel push-pull chromophores, convenient electron acceptor/donor groups (CN and NO_2/NMe_2 and OMe) and moieties (heterocyclic units/ferrocene, etc.) were utilized [21-27]. In addition to our previous TFB-derived chromophores [28], we report herein the synthesis of four novel TFB-derived quadrupolar D-π-A-π-D molecules **1a**-**b** and **2a**-**b** (Fig. 1) with two peripheral *O*-hexyloxy and *N*,*N*-dihexylamino groups connected *via* a π-conjugated system composed of 1,4-phenylene, 2,5-thienylene and acetylenic subunits. Whereas the central TFB unit polarizes the π-system *via* its overall electron withdrawing character, the peripheral *O*-hexyloxy and *N*,*N*-dihexylamino groups behave as electron donors. Moreover, due to the presence of long hexyl chains, target chromophores **1a**-**b** and **2a**-**b** showed enhanced solubility in common organic solvents.

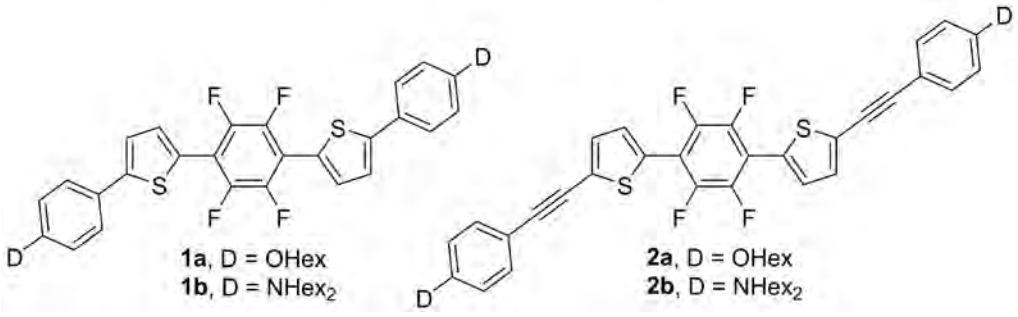


Fig. 1 General structure of target quadrupolar chromophores **1a**-**b** and **2a**-**b**

Experimental

General

All reactions were carried out in a vacuum-dried Schlenk flask under Ar. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 360 nm). Melting points (m.p.) were measured in open capillaries and were uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400, 100 and 376 MHz at 25 °C with a Bruker AVANCE 400 instrument. Chemical shifts in ^{1}H, ^{13}C and ^{19}F NMR spectra are reported in ppm relative to the signal of Me_4Si (0.00 ppm) and C_6F_6 (–164.90 ppm). The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ 7.25 and 77.23 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet), and m (multiplet). ^{1}H NMR signals of 1,4-phenylene/2,5-thienylene moieties were denoted as Ph/Th. Signals of some quaternary carbons are missing in ^{13}C NMR due to broad C-F interaction. Two sets of signals were observed for **2a** as a result of the presence of two rotamers. EI-MS spectra were measured on a GC/MS configuration comprised of an Agilent Technologies 6890N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33-550 Da). High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (m/z 50-1500) with the following setting of tuning parameters: resolution 100,000 at m/z = 400, laser energy 17 mJ, number of laser shots 5. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width $\Delta m/z$ 4, normalized collision energy 25 %, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for CID experiments in LTQ linear ion trap. The used matrix was 2,5-dihydroxybenzoic acid (DHB). The mass spectra were averaged over the whole MS record (30 s) for all the measured samples.

General Method for Suzuki–Miyaura Cross-coupling Reaction (**1a/b**-**2a/b**)

1,4-Diiodotetrafluorobenzene (401.9 mg, 1.0 mmol) or 1,4-bis(5-bromothiophene-2-yl)tetrafluorobenzene (472.1 mg, 1.0 mmol) [30] and appropriate boronic acid pinacol ester (2.5 mmol) were dissolved in the mixture of THF/H_2O (50 ml, 4:1). Argon was bubbled through the solution for 10 min, whereupon [$PdCl_2(PPh_3)_2$] (98.3 mg, 0.14 mmol) and Na_2CO_3 (318 mg, 3.0 mmol) were added and the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (2×50 ml). The combined organic

extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo*, and the crude product was purified by twofold decantation from dichloromethane/hexane (1:2) or column chromatography (SiO_2; solvent CH_2Cl_2/hexane 1:20).

Target Chromophore **1a**

Compound **1a** was synthesized from 1,4-bis(5-bromothiophene-2-yl)tetrafluorobenzene according to the general method for Suzuki–Miyaura cross-coupling reaction and using boronic acid pinacol ester **3a**. Yield 250 mg (36 %) of greenish solid, m.p. 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, 6H, *J* = 7.0 Hz, 2×CH_3), 1.32-1.37 (m, 8H, 4×CH_2), 1.43-1.49 (m, 4H, 2×CH_2), 1.79-1.83 (m, 4H, 2×CH_2), 3.99 (t, 4H, *J* = 6.6 Hz, 2×OCH_2), 6.93 (d, 4H, *J* = 8.8 Hz, 2×Ph), 7.27 (d, 2H, *J* = 3.9 Hz, 2×Th), 7.58 (d, 4H, *J* = 8.8 Hz, 2×Ph), 7.62 (d, 2H, *J* = 3.9 Hz, 2×Th) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.27, 22.83, 25.94, 29.42, 31.81, 68.38, 115.22, 122.50, 126.34, 127.51, 131.56, 159.59 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –144.16 ppm. HR-MALDI-MS, *m/z*: calcd. for $C_{38}H_{38}O_2S_2F_4^+$ 666.2244 $[M]^+$; found 666.2259.

Target Chromophore **1b**

Compound **1b** was synthesized from 1,4-bis(5-bromothiophene-2-yl)tetrafluorobenzene according to the general method for Suzuki–Miyaura cross-coupling reaction and using boronic acid pinacol ester **3b**. Yield 416 mg (50 %) of orange solid, m.p. 143-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 12H, *J* = 6.6 Hz, 4×CH_3), 1.29-1.36 (m, 24H, 12×CH_2), 1.55-1.63 (m, 8H, 4×CH_2), 3.29 (t, 8H, *J* = 7.6 Hz, 4×NCH_2), 6.63 (d, 4H, *J* = 9.2 Hz, 2×Ph), 7.18 (d, 2H, *J* = 4.0 Hz, 2×Th), 7.50 (d, 4H, *J* = 9.2 Hz, 2×Ph), 7.61 (d, 2H, *J* = 4.0 Hz, 2×Th) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.29, 22.93, 27.06, 27.46, 31.95, 51.30, 111.82, 120.74, 120.86, 124.96, 127.37, 131.43, 142.86, 145.32, 148.30, 148.53 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –144.61 ppm. HR-MALDI-MS, *m/z*: calcd. for $C_{50}H_{64}N_2S_2F_4^+$ 832.4442 $[M]^+$; found 832.4484.

Target Chromophore **2a**

Compound **2a** was synthesized from 1,4-diiodotetrafluorobenzene and according to the general method for Suzuki–Miyaura cross-coupling reaction and using boronic acid pinacol ester **4a**. Yield 378 mg (53 %) of green-brown solid, m.p. 147-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 6H, *J* = 7.0 Hz, 2×CH_3),

1.31-1.35 (m, 8H, 4×CH_2), 1.43-1.47 (m, 4H, 2×CH_2), 1.76-1.80 (m, 4H, 2×CH_2), 3.95-3.98 (m, 4H, 2×OCH_2), 6.84-6.88 (m, 4H, 2×Ph), 7.04+7.11 (d, 2H, J = 3.8 Hz, 2×Th), 7.27+7.58 (d, 2H, J = 3.8 Hz, 2×Th), 7.41-7.46 (m, 4H, 2×Ph), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.26, 22.82, 25.91, 29.35, 31.78, 68.32, 80.80+81.36, 94.88, 96.24, 114.46+114.69, 114.79+114.83, 123.15, 124.02, 127.05, 128.74, 137.87, 131.64, 133.12+133.24, 159.70+159.87 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –143.55 ppm. HR-MALDI-MS, *m*/*z*: calcd. for $C_{42}H_{38}O_2S_2F_4^+$ 714.2244 $[M]^+$; found 714.2244.

Target Chromophore **2b**

Compound **2b** was synthesized from 1,4-diiodotetrafluorobenzene according to the general method for Suzuki–Miyaura cross-coupling reaction and using boronic acid pinacol ester **4b**. Final purification was carried out by column chromatography (SiO_2; hexane/CH_2Cl_2 20:1). Yield 194 mg (22 %) of orange solid, m.p. 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 12H, J = 6.4 Hz, 4×CH_3), 1.26-1.34 (m, 24H, 12×CH_2), 1.51-1.61 (m, 8H, 4×CH_2), 3.26 (t, 8H, J = 7.6 Hz, 4×NCH_2), 6.54 (d, 4H, J = 9.0 Hz, 2×Ph), 7.02 (d, 2H, J = 3.8 Hz, 2×Th), 7.06 (d, 2H, J = 3.8 Hz, 2×Th), 7.32 (d, 4H, J = 9.0 Hz, 2×Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.29, 22.90, 27.00, 27.35, 31.91, 51.15, 80.50, 96.31, 111.29, 123.74, 123.77, 131.71, 132.97, 137.35, 148.26 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –145.57 ppm. HR-MALDI-MS, *m*/*z*: calcd. for $C_{54}H_{64}N_2S_2F_4^+$ 880.4442 $[M]^+$; found 880.4489.

General Method for Synthesis of Boronic Acid Pinacol Esters (**3a/b-4a/b**)

A solution of iodo compound or thiophene derivative **5a**/**b** (3.0 mmol) in dry THF (100 ml) was treated with *n*BuLi (1.94 ml, 3.1 mmol; 1.6 M sol. in hexane) or lithium di*iso*propylamide (1.55 ml, 3.1 mmol; 2 M sol. THF/heptane/ethylbenzene; LDA) at –78 °C under argon for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.63 ml, 3.1 mmol; *i*PrOBpin) was added, and the reaction mixture was allowed to reach 25 °C and was stirred for 1 h. NH_4Cl (sat. aq. sol.) was added, the reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (2×50 ml). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo*, and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2/hexane 1:1).

Compound **3a**

Compound **3a** was synthesized from 1-hexyloxy-4-iodobenzene by following the general method for the synthesis of boronic acid pinacol esters. Yield 885 mg (97 %) of off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 3H, *J* = 7.0 Hz, CH_3), 1.28-1.33 (m, 4H, 2×CH_2), 1.43-1.47 (m, 2H, CH_2), 1.74-1.81 (m, 2H, CH_2), 3.97 (t, 2H, *J* = 6.6 Hz, OCH_2), 6.88 (d, 2H, *J* = 8.7 Hz, Ph), 7.74 (d, 2H, *J* = 8.7 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.22, 22.78, 25.03, 25.88, 29.35, 31.76, 67.93, 83.66, 114.01, 136.66, 161.93 ppm. EI-MS 70 eV, *m*/*z* (rel. int.): 304 (42, $[M]^+$), 220 (38), 205 (100), 134 (54), 121 (50), 43 (46).

Compound **3b**

Compound **3b** was synthesized from *N*,*N*-dihexyl-4-iodoaniline by following the general method for the synthesis of boronic acid pinacol esters. Yield 789 mg (68 %) of off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 3H, *J* = 7.0 Hz, CH_3), 1.24-1.31 (m, 12H, 3×CH_2), 1.48-1.56 (m, 4H, 2×CH_2), 3.27 (t, 4H, *J* = 7.6 Hz, NCH_2), 6.59 (d, 2H, *J* = 8.8 Hz, Ph), 7.64 (d, 2H, *J* = 8.8 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.25, 22.86, 25.00, 26.99, 27.35, 31.91, 51.00, 83.22, 110.76, 136.49, 150.46 ppm. EI-MS 70 eV, *m*/*z* (rel. int.): 387 (22, $[M]^+$), 316 (100), 246 (38).

Compound **4a**

Compound **4a** was synthesized from **5a** by following the general method for the synthesis of boronic acid pinacol esters. Compound **4a** proved to be unstable and should be used immediately in the next reaction step. Yield 246 mg (20 %) of oil. EI-MS 70 eV, *m*/*z* (rel. int.): 410 (80, $[M]^+$), 326 (70), 226 (68), 43 (100).

Compound **4b**

Compound **4b** was synthesized from **5b** by following the general method for the synthesis of boronic acid pinacol esters. Compound **4b** proved to be unstable and should be used immediately in the next reaction step. Yield 931 mg (63 %) of oil. EI-MS 70 eV, *m*/*z* (rel. int.): 493 (96, $[M]^+$), 422 (83), 352 (100), 252 (59), 237 (44), 207 (63), 43 (82).

Compound **5a**

Compound **5a** was synthesized from 1-hexyloxy-4-iodobenzene and 2-ethynyl-thiophene by following the general method for Sonogashira cross-coupling reaction given in reference [28]. Yield 48 %, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, 3H, *J* = 7.0 Hz, CH_3), 1.40-1.44 (m, 4H, 2×CH_2), 1.52-1.56 (m, 2H, CH_2), 1.82-1.90 (m, 2H, CH_2), 4.04 (t, 2H, *J* = 6.6 Hz, OCH_2), 6.94 (d, 2H, *J* = 8.8 Hz, Ph), 7.07 (dd, 1H, *J* = 3.7 and 5.0 Hz, Th), 7.31-7.34 (m, 2H, Th), 7.52 (d, 2H, *J* = 8.8 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.24, 22.80, 25.88, 29.34, 31.76, 68.24, 81.34, 93.34, 114.72, 114.86, 123.94, 126.94, 127.21, 131.56, 133.08, 159.54 ppm. EI-MS 70 eV, *m*/*z* (rel. int.): 284 (42, $[M]^+$), 200 (100), 171 (22).

Compound **5b**

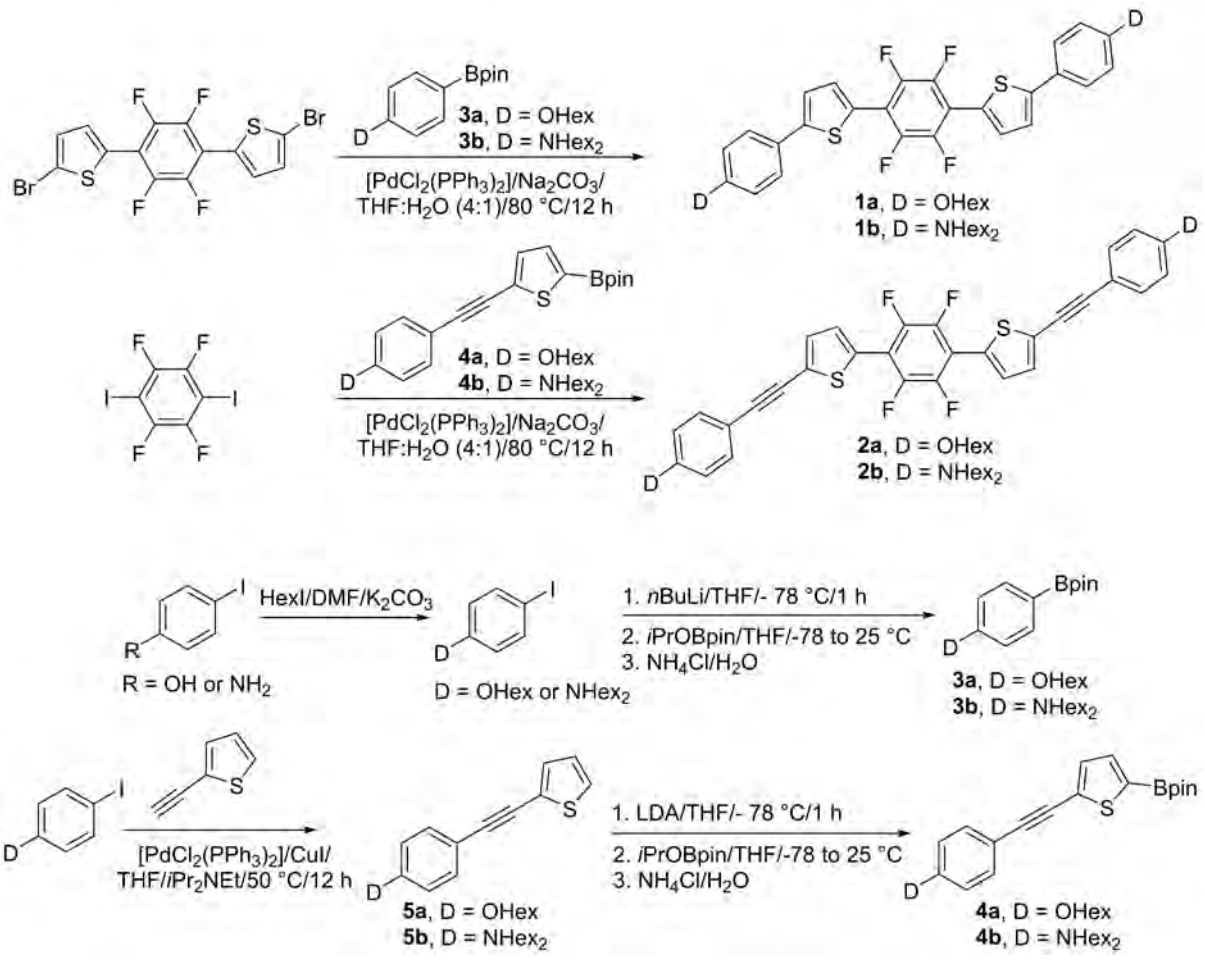
Compound **5b** was synthesized from *N*,*N*-dihexyl-4-iodoaniline and 2-ethynyl-thiophene by following the general method for Sonogashira cross-coupling reaction given in reference [28] . Yield 46 %, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, 6H, *J* = 6.7 Hz, 2×CH_3), 1.30-1.35 (m, 12H, 6×CH_2), 1.55-1.59 (m, 4H, 2×CH_2), 3.28 (t, 4H, *J* = 7.8 Hz, 2×NCH_2), 6.57 (d, 2H, *J* = 9.0 Hz, Ph), 6.98 (dd, 1H, *J* = 3.7 and 5.0 Hz, Th), 7.20-7.22 (m, 2H, Th), 7.36 (d, 2H, *J* = 9.0 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.32, 22.95, 27.04, 27.41, 31.86, 51.18, 80.35, 94.81, 108.40, 111.35, 124.82, 126.29, 127.17, 130.89, 133.00, 148.25 ppm. EI-MS 70 eV, *m*/*z* (rel. int.): 367 (68, $[M]^+$), 296 (99), 226 (100), 212 (45), 184 (33), 139 (28), 113 (37).

Results and Discussion

Synthesis

The synthesis of target compounds **1a**-**b** and **2a**-**b** has been accomplished *via* twofold Suzuki–Miyaura cross-coupling reaction of the donor-substituted π-linkers **3a**-**b** and **4a**-**b** with 1,4-bis(5-bromothiophene-2-yl)tetrafluorobenzene [29] and commercially available 1,4-diiodotetrafluorobenzene (Scheme 1). The syntheses of starting boronic acid pinacol esters **3a**-**b** and **4a**-**b** are also outlined in Scheme 1. The reaction sequence involves *O*- and *N*,*N*-(di)hexylation of 4-iodophenole and 4-iodoaniline using iodohexane and K_2CO_3 in DMF [30] and subsequent lithiation with *n*BuLi and the reaction with *i*PrOBpin [31] to afford intermediates **3a**-**b** with the yields of 97 and 68 %. *O*- and *N*,*N*-(di)hexylated 4-iodophenole and 4-iodoanilne were subsequently treated with 2-ethynyl-

thiophene in terms of Sonogashira reaction [28] to afford intermediates **5a-b** with the yields 48 and 46 %. These were further lithiated with LDA and subsequently reacted with *i*PrOBpin [31] to afford desired boronic acid pinacol esters **4a-b** with the yields of 20 and 63 %. However, these two compounds proved to be unstable and partially decompose during column chromatography or storing and, therefore, were used directly in the next reaction step without proper purification. Table I shows the type of appended donor group, yield of the final cross-coupling step, melting points and the characterization performed for all target compounds **1a-b** and **2a-b**.



Scheme 1 Reaction sequence leading to target chromophores **1a-b** and **2a-b**

Characterization

Structural characterizations of intermediates **3-5** were accomplished by ^{1}H and ^{13}C NMR spectroscopy as well as by GC/MS analysis (see Experimental). Intermediates **4a** and **4b** were characterized only by GC/MS analysis due to their instability. Thorough structural analysis were carried out for target compounds

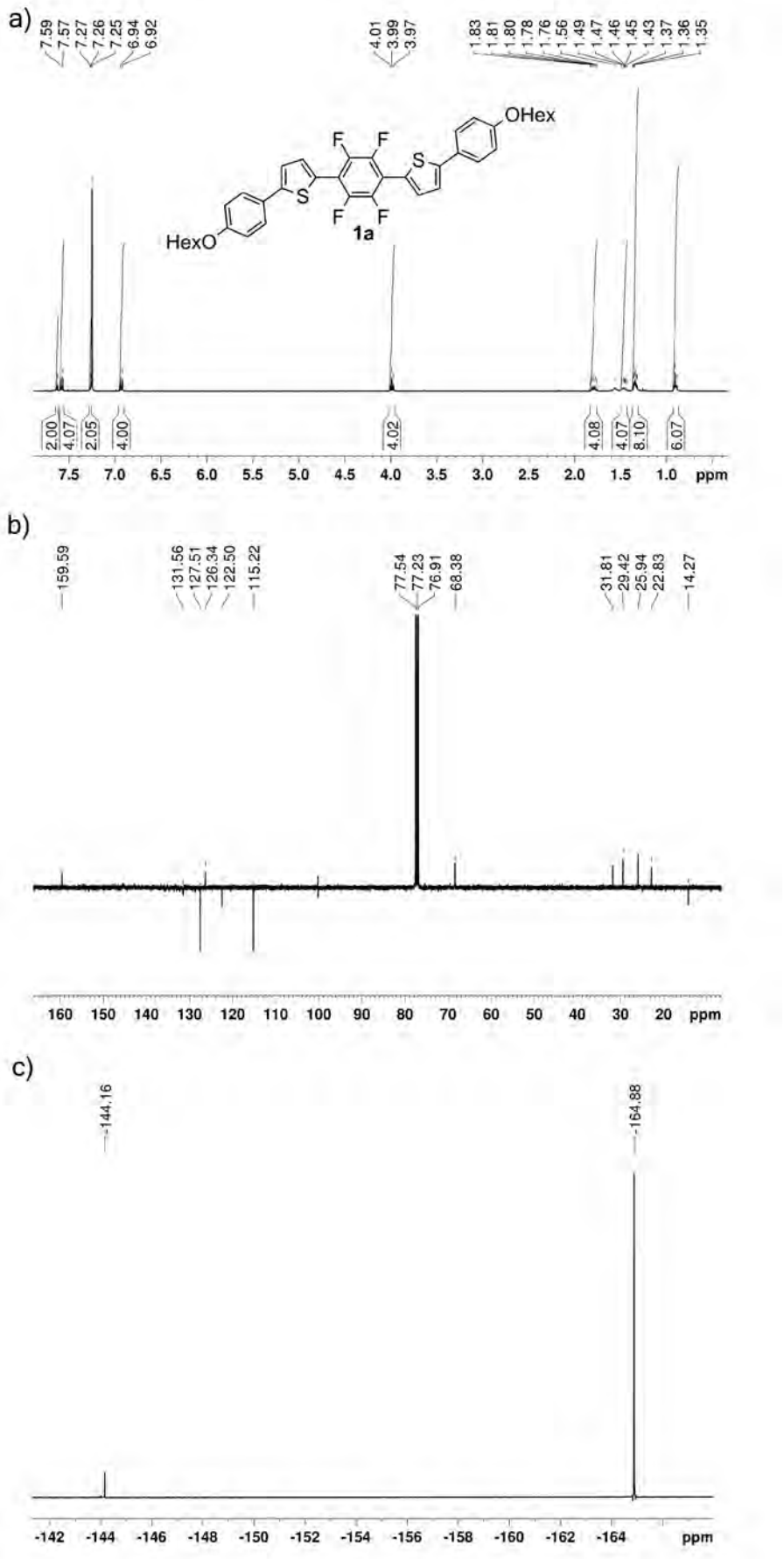


Fig. 2 Representative ^{1}H (a), ^{13}C APT (b) and ^{19}F (c) NMR spectra of chromophore **1a**

Table I Structure, yields, melting points and characterization of target chromophores **1a**-**b** and **2a**-**b**

Comp.	D	Yield %	Mp °C	Characterization
1a	OHex	36	184–186	^{1}H, ^{13}C, ^{19}F NMR; HR-MALDI-MS
1b	$NHex_2$	50	143–146	^{1}H, ^{13}C, ^{19}F NMR; HR-MALDI-MS
2a	OHex	53	147–150	^{1}H, ^{13}C, ^{19}F NMR; HR-MALDI-MS
2b	$NHex_2$	22	104–105	^{1}H, ^{13}C, ^{19}F NMR; HR-MALDI-MS

1a-**b** and **2a**-**b**. These compounds were characterized by melting points, ^{1}H, ^{13}C (APT) and ^{19}F NMR spectra and by high resolution MALDI mass spectra (HR-MALDI-MS). The representative NMR spectra of derivatives **1a** and **2b** are shown in Figs 2 and 3. Both molecules are centrosymmetric and, therefore, their NMR spectra showed one set of signals for both halves of the molecule. The ^{1}H NMR of **1a** spectra consists of a set of up-fielded signals of the OHex substituents appearing at 0.91-3.99 ppm and showing a pattern (spin-spin interaction) typical of hexyl chain (Fig. 2). The downfield region of the spectra showed the signals of the 1,4-phenylene moieties appearing at 6.93 and 7.58 ppm (set of two doublets with J = 8.8 Hz) and two narrow doublets of the 2,5-thienylene unit at 7.27 and 7.62 ppm with J = 3.9 Hz, respectively.The ^{13}C APT NMR spectrum showed the expected signals prevailingly of CH_3, CH_2 and CH groups, four signals of tertiary carbon atoms were missing due to a limited solubility of **1a** in $CDCl_3$ and ^{13}C-^{19}F interaction. The ^{19}F NMR spectrum showed only one signal at –144.16 ppm which further demonstrates centrosymmetry of **1a**. The HR-MALDI-MS spectrum showed peak at m/z = 666.2259 Da which conforms to structure of **1a** having sum formula $C_{38}H_{38}O_2S_2F_4^+$ and exact mass of 666.2244 Da.

In contrast to **1a**, the ^{1}H NMR spectrum of **2b** is dominated by four signals of the $NHex_2$ group appearing in the upfield region between 0.89 and 3.26 ppm (Fig. 2). The multiplicities and integrals correspond to two dihexyl chains. The aromatic region of the ^{1}H NMR spectra of **2b** showed a pattern different from that of **1a**, namely two doublets of the 1,4-phenylene moieties (6.54 and 7.32 with J = 9.0 Hz) and two narrow doublets in between (7.02 and 7.06 with J = 3.8 Hz). These signals correspond to two 2,5-thienylene moieties. The different pattern results from the attachment of *N*,*N*-dihexylamino donor and extension of the π-conjugated path by acetylenic unit. The presence of the acetylenic unit in **2b** can also be visualized by the ^{13}C APT NMR spectrum showing two distinguishable signals at 80.50 and 96.31 ppm. As expected, the ^{19}F NMR spectrum showed one signal at –145.57 ppm. The HR-MALDI-MS spectrum showed a peak at m/z = 880.4489 Da which conforms to structure of **2b** having sum formula $C_{54}H_{64}N_2S_2F_4^+$ and the exact mass of 880.4442 Da.

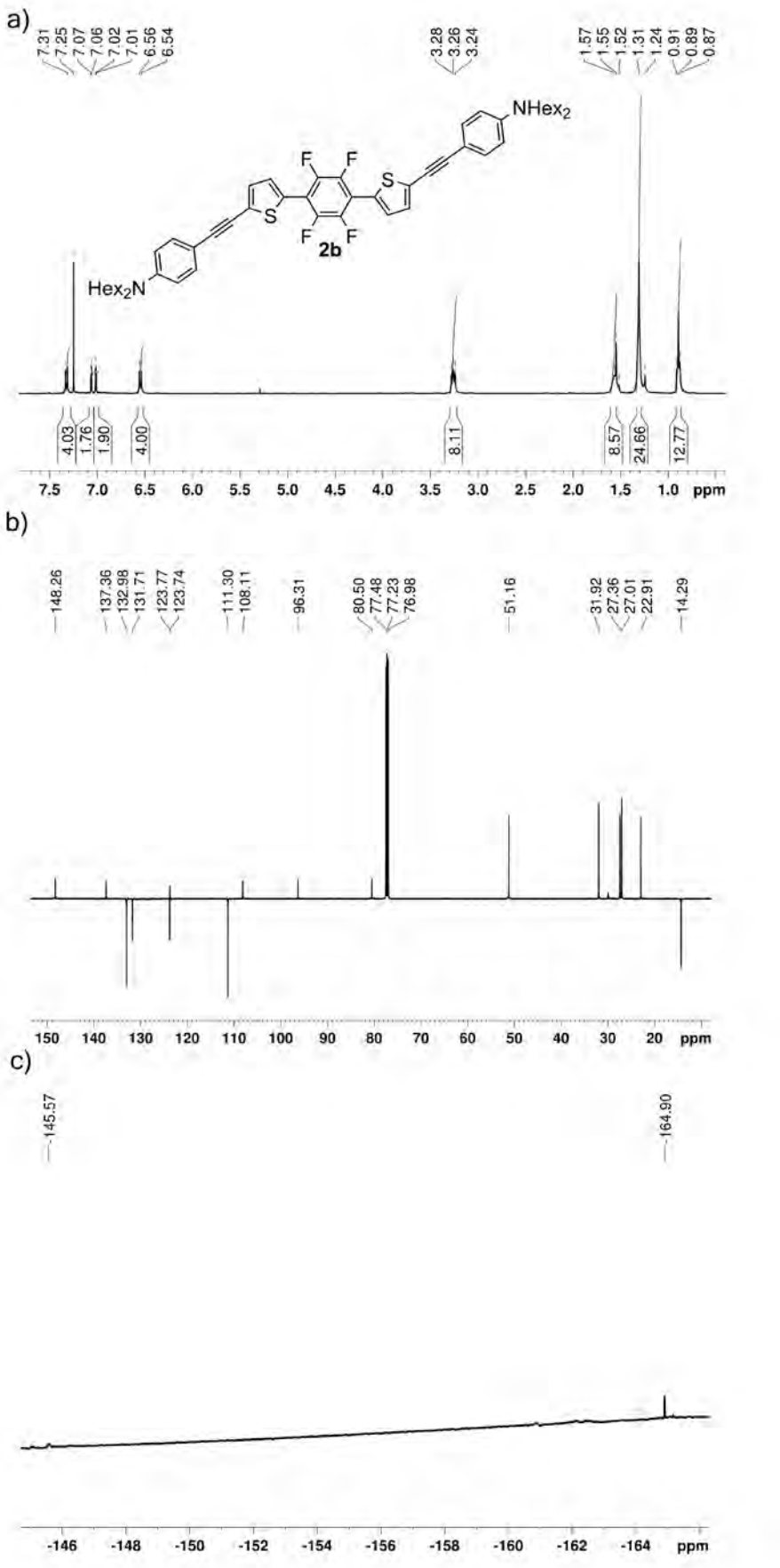


Fig. 3 Representative ^{1}H (a), ^{13}C APT (b) and ^{19}F (c) NMR spectra of chromophore **2b**

Conclusion

Two new types of quadrupolar D-π-A-π-D chromophores with central tetrafluorobenzene acceptor unit and two peripheral hexyloxy and *N*,*N*-dihexylamino donor groups were synthesized. The π-conjugated system comprises a combination of 1,4-phenylene and 2,5-thienylene units (chromophores **1a**/**b**) as well as an additional triple bond spacer (chromophores **2a**/**b**). The synthesis started from *O*- and *N*,*N*-(di)hexyaltion of 4-iodophenole and 4-iodoaniline, their lithiation and reaction with *i*PrOBpin and subsequent cross-coupling reaction of the prepared boronic acid pinacol esters **3a**/**b** with 1,4-bis(5-bromothiophene-2-yl)tetrafluorobenzene to afford chromophores **1a**/**b**. Chromophores **2a**/**b** with extended π-system were synthesized from (di)hexylated 4-iodophenole and 4-iodoaniline and their Sonogashira cross-coupling with 2-ethynylthiophene. The subsequent lithiation and reaction with *i*PrOBpin afforded unstable boronic acid pinacol esters **4a**/**b** that were immediately treated with 1,4-diiodotetrafluorobenzene in terms of Suzuki–Miyaura cross-coupling providing target chromophores **2a**/**b**. In this way, chromophores **1** and **2** were obtained in 22-53% yields. Structural analysis was carried out by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy as well as by HR-MALDI-MS. All the measured data conform to the proposed structure.

Acknowledgement

M.R. is indebted to the Ministry of Education, Youth and Sports of the Czech Republic (CZ.1.07/2.3.00/30.0021).

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