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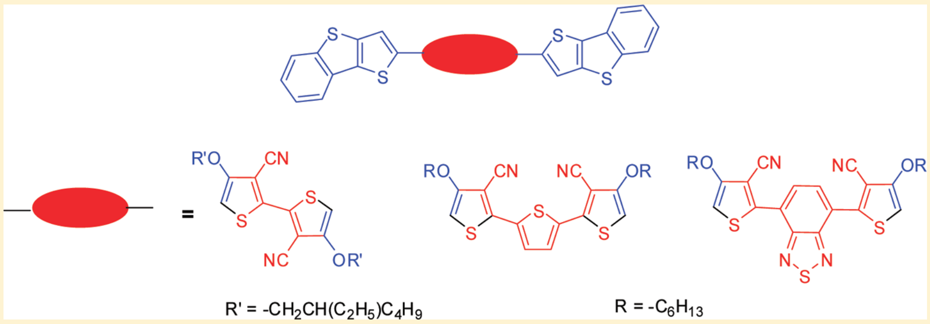
Synthesis and Electronic Properties of D–A–D Triads Based on 3-Alkoxy-4-cyanothiophene and Benzothienothiophene Blocks

Charlotte Mallet,[†] Gurunathan Savitha,[†] Magali Allain,[†] Václav Kozmík,[‡] Jiří Svoboda,[‡] Pierre Frère,*[,†] and Jean Roncali[†]

[†]LUNAM Université, Moltech Anjou CNRS UMR 6200, Group Linear Conjugated Systems, 2 Boulevard Lavoisier, 49045 Angers Cedex, France

[‡] Department of Organic Chemistry, Institute of Chemical Technology Prague, Technicka 5, CZ-166 28 6 Praha 6, Czech Republic

Supporting Information



ABSTRACT: 3-Alkoxy-4-cyanothiophene units are used as building block for the synthesis of conjugated donor–acceptor–donor (D–A–D) triads. The donor part consists of benzothienothiophene end groups associated with the alkoxy groups of the 3-alkoxy-4-cyanothiophene, while the central acceptor part is formed by combining the electron-withdrawing cyano group with thiophene or benzothiadiazole units.

Thiophene-based conjugated materials represent one of the most widely investigated classes of functional π-conjugated systems[1,2] because of their potential technological applications as active materials for the fabrication of organic (opto)electronic devices such as field-effect transistors (OFETs), electroluminescent diodes (OLEDs), and photovoltaic cells (OPVs).[3−7]Appropriate modifications of the conjugated backbone allow the control of the energy levels of the HOMO and LUMO frontier orbitals and thus the tuning of the bandgap and electronic properties of the resulting materials.[8−10]

Various synthetic strategies can be used to control the energy levels and band gap of π-conjugated systems including covalent or noncovalent rigidification of the conjugated system,[11−15] quinoidization,[16] or the creation of alternating donor (D) and acceptor (A) blocks.[17−19] In this context, the D/A approach has attracted particular interest due to a combination of efficiency and versatility allowing multiple possibilities of combination of D and A building blocks.[20−22] In fact, most of the low band gap polymers used as donor materials in highly efficient organic solar cells have been designed on the basis of the D/A approach.[23,24]

On the other hand, recent years have seen the emergence of soluble small conjugated molecules as donor material for solution-processed organic solar cells.[6,9] In this context, triad molecules based on the D–A–D or A–D–A architecture have been shown to lead to interesting performances as donor materials in organic solar cells.[25−31]

We have previously reported that 3-alkoxy-4-cyanothiophenes represent original building block.[32,33] The presence of donor and acceptor substituents grafted on the same thiophene unit ensures maximum D/A interactions, which is not necessarily the case when D and A blocks are connected by a single bond subject to possible rotational disorder.

We report here on the synthesis and characterization of the optical and electrochemical properties of new D–A–D triads **BTn** in which the ambivalent structure of 3-alkoxy-4-cyanothiophenes units is used to create the central electron-acceptor block either by direct connection of the 5,5′ positions of 3-alkoxy-4-cyanothiophenes or by association with other moieties such as thiophene or benzothiadiazole (Figure 1).

The median blocks with the acceptor groups and the final target molecules have been synthesized by Stille coupling reactions as shown in Scheme 1. The *n*-BuLi/Me$_3$SnCl sequence on the 3-alkoxy-4-cyanothiophene **1** gave the stannic derivative **2** with selective metalation at the position adjacent to the cyano group.[32] An oxidative coupling of **2** using 0.5 equiv of I$_2$ and catalytic amount of CuCl$_2$ (10% molar) led to dimer **3** in 35% yield. It should be noted that the direct oxidative coupling of the lithiated derivative of **1** gave the dimer in less than 10% yield. The trimers **5** and **7** were prepared by a 2-fold Stille

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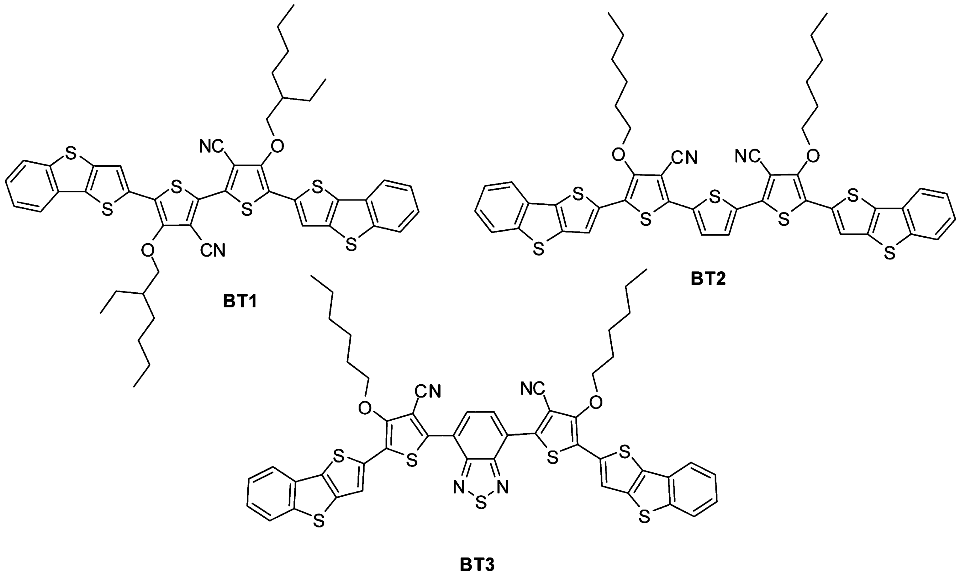
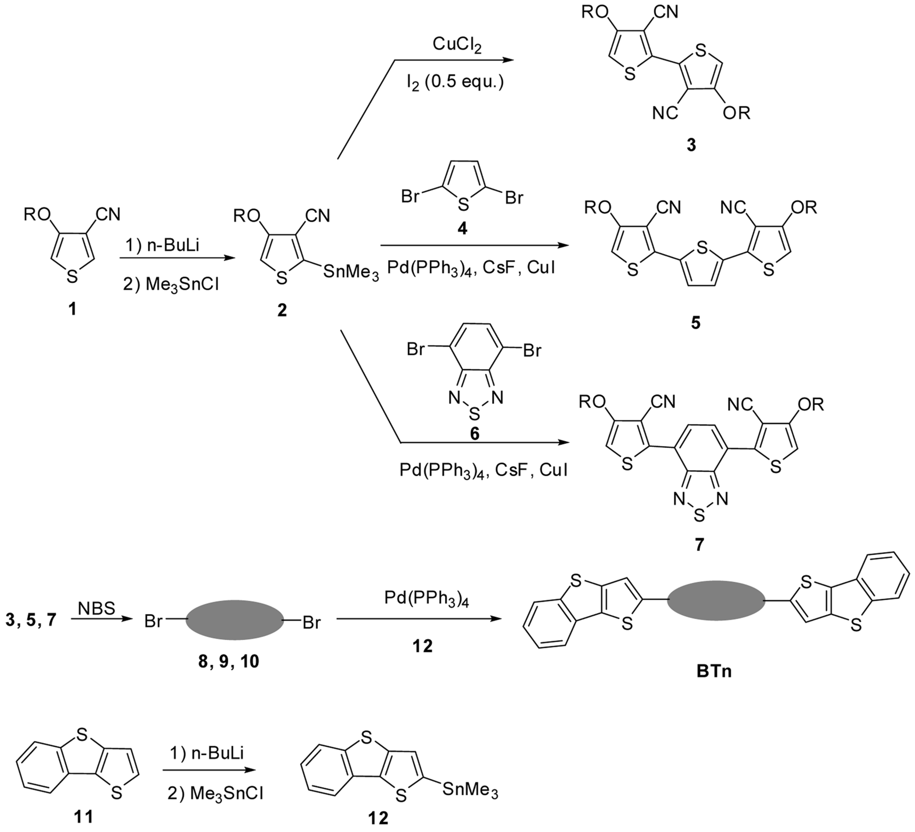


Figure 1. Structures of D−A−D triads **BTn**.

Scheme 1. Synthetic Pathway of the Triads BTn



coupling reaction between dibromothiophene **4** or dibromobenzothiadiazole **6** and the stannyl derivative **2**. The coupling reaction using only $Pd(PPh_3)_4$ (10% mol) as catalyst gave the trimers in less than 20% yield. Recently, Baldwin et al. showed that the combined addition of CuI and CsF strongly improved transmetalation by allowing the in situ formation of more reactive copper derivative.[34,35] Thus, following this protocol, trimers **5** and **7** have been obtained in 67% and 83% yield, respectively. Treatment of **3**, **5**, and **7** by NBS gave the corresponding brominated derivatives **8**, **9**, and **10** in 75−80% yields.

Thieno[3,2-*b*][1]benzothiophene **11** was obtained in five steps from thiosalicylic acid as previously described.[36] The trimethylstannyl derivative of benzothienothiophene **12**, quantitatively prepared by the BuLi/Me_3SiCl sequence, was coupled with the dibrominated compounds **8**, **9**, and **10** to give the target molecules **BTn** in 42−67% yield.

The crystallographic structures of single crystals of the spacers **5** and **7** have been analyzed by X-ray diffraction. Compound **5** crystallizes in the monoclinic C1/c space group. The conformation adopted by the molecules in the crystal associates a *δsyn* orientation of a terminal thiophene with the central thiophene cycle and a *δtrans* with the other (Figure 2). The two *δsyn* thiophenes are coplanar while the third presents a dihedral torsion of 11°. The two hexyl chains are located above and below the plane formed by the conjugated system. The molecules stack along the *b* axis by developing a self-organizing through lipophilic interactions between the hexyl chains and $\pi-\pi$ interactions between the conjugated systems (Figure S1, Supporting Information). The average distance between the planes formed by the thiophenes is 3.7 Å, but the slight shift of the thiophene cycles does not allow the formation of S---S intermolecular interactions.

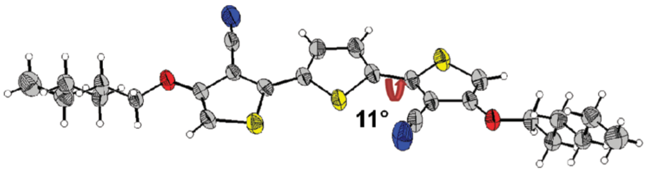


Figure 2. X-ray structure of **5**. Molecular structure of **5** with anisotropic displacement ellipsoids drawn at the 50% probability level.

Compound **7** crystallizes in the triclinic *P*-1 space group. The three heterocyclic moieties are perfectly coplanar with the two sulfur atoms of the thiophenes pointing to the nitrogen atoms of the central benzothiadazole unit (Figure 3). The inter atomic S---N distances of 2.77 Å and 2.80 Å are considerably shorter than the sum of the van der Waals radii of sulfur and nitrogen (3.39 Å), thus indicating the occurrence of noncovalent S---N intramolecular interactions that stabilize the planar conformation.[19] The two hexyl branches point perpendicularly to the plane defined by the heterocycles. The stacking of the molecules along the *a* axis presents an overlapping of the molecular planes with a slight shift, so that a benzothiadiazole moiety is placed opposite to a thiophene ring (Figure S2, Supporting Information). The average distance between the conjugated systems is approximately of 3.4 Å which corresponds to classical distances for $\pi-\pi$ interactions.

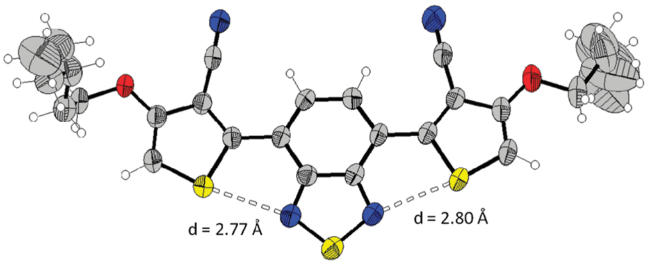


Figure 3. X-ray structure of **7**. Molecular structure of **7** with anisotropic displacement ellipsoids drawn at the 50% probability level.

To analyze in more detail the influence of the structure on the electronic properties of oligomers, theoretical calculations were performed at the ab initio density functional level with the Gaussian 09 package. Becke's three-parameter gradient-corrected functional (B3LYP) with a polarized 6-31G (d,p) basis was used for full geometry optimization of compounds **BTn**. The hexyloxy are replaced by ethyloxy groups in order to reduce computation time. The calculated HOMO and LUMO levels and the gap ΔE_{th} are gathered in Table 1. The contours of the HOMO and LUMO orbitals and a schematic evolution of their levels are shown in Figure 4. The structure of **BT1** shows a fully planar conformation with the two central thiophene units in a *δtrans* conformation, in agreement with the crystallographic structure of the dimer **3**.[32] The energy minimum corresponds to a *δtrans* conformation of the benzothienothiophene units with the adjacent thiophene. As often observed in oligothiophenes bearing alkoxy groups, this conformation is stabilized by S---O intramolecular interactions.[15,37] The HOMO of **BT1** resides wholly on the conjugated backbones while the LUMO is localized on the acceptor middle part. The lengthening of this part by insertion of a thiophene cycle is accompanied by a slight torsion of the spacer for **BT2**. The energy minimum was obtained for a conformation with the three central thiophene cycles in a *δcis* conformation. The torsion angle between two adjacent thiophenes is about 16−18° while in the *δtrans* conformation this angle reaches 25°. This result agrees with the crystal structure of the compound **5** which shows a larger torsion angle for the two thiophenes in a *δtrans* than in a *δcis* conformation. As for **BT1**, the benzothienothiophene units are coplanar with the adjacent thiophenes. Here also the HOMO is delocalized on the whole conjugated systems while the LUMO is localized on the central terthiophene units bearing the cyano groups. The small decrease of the energy gap from 2.46 eV for **BT1** to 2.40 eV for **BT2** corresponds to a small destabilization of 0.05 eV of the HOMO level while the LUMOs remain quasi unchanged. Finally the replacement of the central thiophene by a benzothiadiazole (BZT) moiety leads to strong decrease of the gap for **BT3** to 1.97 eV. The electron-withdrawing BZT unit provokes a strong decrease of the LUMO level without strongly affecting the HOMO. The planar conformation of **BT3** is stabilized by S---N intramolecular interactions between the sulfur atoms of thiophene and the nitrogen of BZT units as observed in the X-ray structure of the compound **7**.

Figure 5 displays the UV−vis absorption spectra of the compounds BTn in dichloromethane solution, while the corresponding data as well as fluorescence emission data are listed in Table 1. The spectra show two distinct absorption bands. The profile of the high energy band with a maximum around 360 nm depends of the nature of the acceptor block. This band could be assigned to specific transition involving the alkoxycyanothiophene and benzothienothiophene moieties. The broad bands of

Table 1. HOMO and LUMO Energy Levels and Theoretical Bandgap ΔE_{the} Calculated by DFT Methods, Experimental Absorption and Emission Data, and Cyclic Voltammetric Data of Triads BTn

compd	HOMO[a] (eV)	LUMO[a] (eV)	ΔE_{the}[a] (eV)	λ_{max}[b] (nm)	ΔE_{opt}[c] (eV)	λ_{em}[d] (nm)	Φ[e] (%)	$E_{pa}1$[f] (V)	$E_{pa}2$[f] (V)	$E_{pc}1$[f] (V)	$E_{pc}2$[f] (V)	ΔE_{ele}[g] (V)
BT1	−5.31	−2.85	2.46	329, *471*	2.20	610	82	1.11	1.22	−1.29	−1.64	2.40
BT2	−5.26	−2.86	2.40	327, *485*	2.16	615	16	1.05	1.18	−1.36	−1.57	2.41
BT3	−5.28	−3.31	1.97	323, 340, *524*	1.91	700	10	1.10	1.29	−1.03	−1.37	2.13

[a] B3LYP/6-31G(d,p). [b] 2.10^{-5} M in CH_2Cl_2. [c] Optical bandgap calculated from the edge of the absorption band. [d] 10^{-5} M in CH_2Cl_2. [e] Based on perylene in CH_2Cl_2. [f] 2×10^{-5} M in 0.1 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mVs^{-1}. [g] Electrochemical bandgap $\Delta E_{ele} = E_{pa}1 - E_{pc}1$.

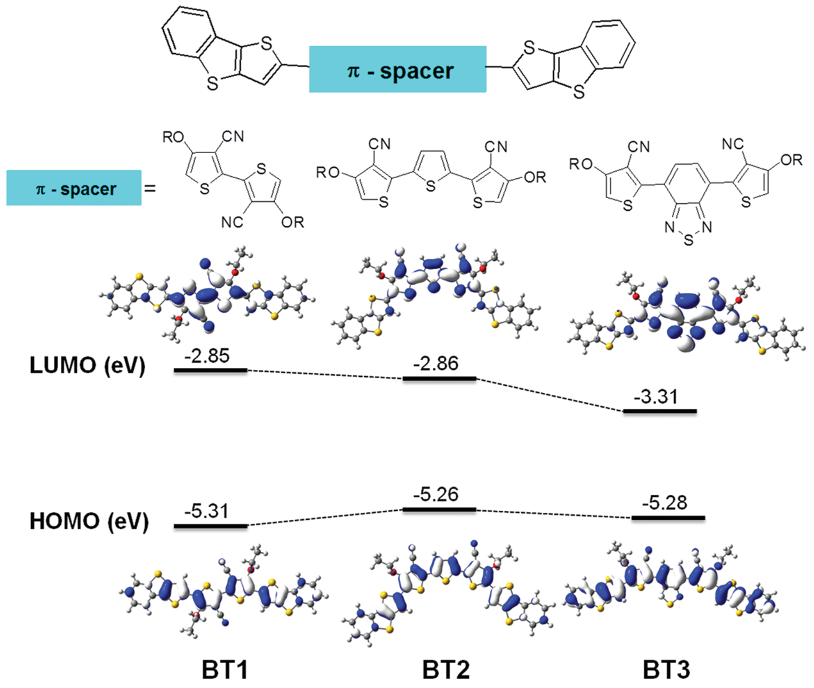


Figure 4. Calculated HOMOs and LUMOs and energy levels for the triads **BTn**.

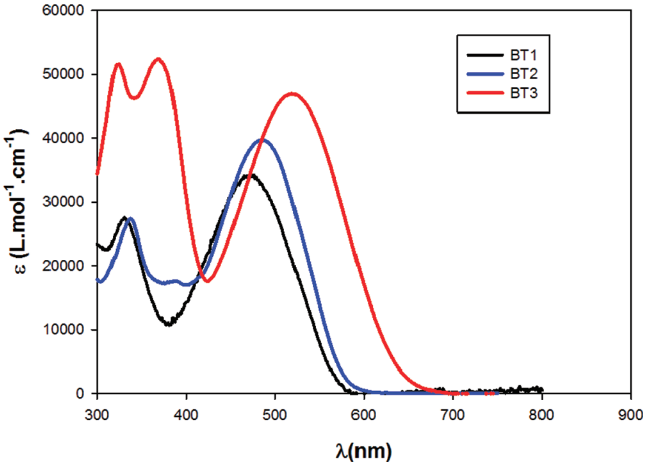


Figure 5. UV−vis absorption spectra of compounds **BTn** in CH_2Cl_2.

lower energy correspond to $\pi-\pi^*$ transitions between the HOMO and LUMO levels of a conjugated systems. The modification of the composition of the acceptor block between **BT1** and **BT2** is accompanied by a 17 nm bathochromic shift of λ_{max} with a 0.11 eV decrease of the HOMO−LUMO gap, in agreement with theoretical calculations. Replacement of the central thiophene by BZT in **BT3** produces a larger red shift of λ_{max} (42 nm).

All compounds fluoresce in CH_2Cl_2 with an emission maximum (λ_{em}) which mainly depends on the structure of the median acceptor block and increases from 610 nm for **BT1** to 700 nm for **BT3**. **BT1** presents the highest fluorescence quantum yield (ϕ_{em}) of 85%. The insertion of an additional thiophene in **BT2** leads to a decrease of ϕ_{em} to 43% while replacement of this thiophene by BZT in **BT3** produces a further decrease of ϕ_{em}.

The electrochemical properties of the **BTn** compounds have been analyzed by cyclic voltammetry (CV), and the oxidation (E_{pa}) and reduction (E_{pc}) potentials are gathered in Table 1. The three compounds **BTn** present two reversible oxidation peaks corresponding to the successive formation of cation radical and dication (Figure S3, Supporting Information). The nature of the acceptor spacer has a small influence on the oxidation potentials that follow the trend indicated by the calculated HOMO levels. Thus, a 60 mV decrease of $E_{pa}1$ is observed between **BT1** and **BT2** while replacement of thiophene by BZT produces a slight increase of E_{pa} indicating that BZT has little influence on the HOMO level.

In the negative potential region, the CV of the three compounds presents two reversible reduction waves corresponding to the formation of the anion radical and dianion. Between **BT1** and **BT2**, the insertion of the thiophene unit provokes a 120 mV negative shift of the first reduction potential ($E_{pc}1$) while replacement by BZT leads to a positive shift of 260 mV for $E_{pc}1$ indicating a strong stabilization of the LUMO.

In conclusion, a new series of conjugated D−A−D triads associating 3-alkoxy-4-cyanothiophene units with the benzothienothiophene moiety have been synthesized. The predominant role of the structure of the spacers for tuning the electronic properties of the compounds has been demonstrated. The HOMO levels are very close, thus conferring to the three derivatives similar electron-donor characters that allow the formation of stable oxidized states. By contrast, the LUMO levels are strongly dependent on the median acceptor structure. The insertion of the BZT unit leads to a strong stabilization of the LUMO level that induces both a decreasing of the band gap and an easier access at the reduced states. These results show that the realization of judicious combinations of 3-alkoxy-4-cyanothiophene unit with electron-donor and -acceptor moieties represents an efficient methodology for the fine-tuning of the electronic properties of extended conjugated systems. On the other hand, the solubility of the D−A−D triads in common solvent, due to the alkoxy chains, is beneficial for developing devices via solution processable techniques, thus suggesting the interest of these compounds as semiconductors materials.

The preparation of photovoltaic cells with these triads is now underway and will be reported in future publications.

■ EXPERIMENTAL SECTION

General Information. ^{1}H NMR and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, with $CDCl_3$ as solvent, and the ^{1}H and ^{13}C chemical shifts were determined by reference to residual nondeuterated solvent resonances (7.26 ppm for ^{1}H NMR and 77.36 ppm for ^{13}C NMR). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration. Cyclic voltammetry was carried out using a platinum disk as the working electrode, platinum wire as the counter electrode, and saturated calomel as the reference electrode.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. 3-Alkoxy-4-cyanothiophenes **2**,[32] dibromobenzothiadiazole **6**,[38] and benzothienothiophene[36] were prepared by procedure described in the literature. 2,5-Dibromothiophene was purchased from commercial sources and used without purification.

2,2′-Bi(3-cyano-4-(2-ethylhexyloxy)thiophene) (3). To a stirred solution of stannyl derivative **2** (1 mmol) in DMF (10 mL) was added 14 mg of $CuCl_2$ (10 mol %). The reaction mixture was heated to reflux at 100 °C, and 127 mg of I_2 (0.5 equiv) in DMF (10 mL) was added dropwise. After addition, reflux was continued until the reaction was complete as monitored by TLC. A saturated solution of KF (50 mL) was added to the reaction mixture, and the product was extracted with dichloromethane (3 × 10 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with petroleum ether and ethyl acetate (9:1) as the eluent to afford compound **3** in 32% yield. Pale yellow crystalline solid. Mp = 78–80 °C. ^{1}H NMR ($CDCl_3$): δ 0.91–0.96 (m, 12H), 1.32–1.58 (m, 16H), 1.74–1.82 (m, 2H), 3.90–3.93 (d, 4H, ^3J = 5.4 Hz), 6.37 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 11.1, 14.1, 22.9, 23.7, 29.0, 30.3, 39.2, 73.6, 99.0, 102.4, 112.9, 139.5, 158.1. MS (MALDI-TOF): $C_{26}H_{36}N_2O_2S_2$ calcd 473.22 (M^+ + 1), found 473.2. Anal. Calcd: C, 66.06; H, 7.68; N, 5.93. Found: C, 66.53; H, 7.71; N, 5.95.

2,5-Bis(3′-cyano-4′-hexyloxy-2′-thienyl)thiophene (5). To a stirred solution of stannyl derivative **2** (835 mg, 3 equiv) and 2,5-dibromothiophene **4** (460 mg, 1.68 mmol) in degassed DMF (5 mL) were added $Pd(PPh_3)_4$ (10 mol %), CuI (20 mol %), and then CsF (1.12 g, 4.4 equiv). The mixture was stirred at 45 °C until the reaction was complete as monitored by TLC. After cooling at rt, the reaction mixture was diluted in water and extracted with dichloromethane, and then the organic phase was dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by a flash chromatography on silica gel (petroleum ether, $CH_2Cl_{2,}$ 1/1) to give 561 mg (67% yield) of compound **4**. Yellow solid. Mp = 140–142 °C. ^{1}H NMR ($CDCl_3$): δ 0.89–0.94 (m, 6H), 1.32–1.37 (m, 8H), 1.46–1.51 (m, 4H), 1.79–1.86 (m, 4H), 4.02 (t, 4H, ^3J = 6.6 Hz), 6.16 (s, 2H), 7.59 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 25.6, 28.8, 31.5, 71.1, 96.4, 99.8, 113.7, 127.6, 135.2, 143.2, 157.8. MS (MALDI-TOF): $C_{26}H_{30}N_2O_2S_3$ calcd 498.1 (M^+), found 498.0. Anal. Calcd: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.17; H, 5.97; N, 5.39.

4,7-Bis(3′-cyano-4′-hexyloxy-2′-thienyl)benzo[*c*][1,2,5]-thiadiazole (7). To a stirred solution of stannyl derivative **2** (418 mg, 2.5 equiv) and dibromobenzothiadiazole **6** (294 mg, 1 mmol) in degassed DMF (5 mL) were added $Pd(PPh_3)_4$ (10 mol %), CuI (20 mol %), and then CsF (670 mg, 4.4 equiv). As examined by TLC, the reaction was completed within 3 min of stirring at rt. The reaction mixture was poured into water and extracted with dichloromethane, and then the organic phase was dried with $MgSO_4$ and removed under vacuum. After evaporation of the solvent, the residue was purified by a flash chromatography on silica gel (petroleum ether, $CH_2Cl_{2,}$ 1/1) and gave 512 mg of (83% yield) 7. Red solid. Mp = 90–92 °C. ^{1}H NMR ($CDCl_3$): δ 0.90–0.95 (m, 6H), 1.34–1.40 (m, 8H), 1.51–1.55 (m, 4H), 1.85 1.90 (m, 4H), 4.08 (t, 4H, ^3J = 6.6 Hz), 6.50 (s, 2H), 8.36 (s, 2H).^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 25.6, 28.9, 31.5, 71.2, 100.3, 102.0, 114.0, 125.4, 128.2, 144.6, 152.3, 158.3. MS (MALDI-TOF): $C_{28}H_{30}N_4O_2S_3$ calcd 551.1 (M^+ + H), found 551.9. Anal. Calcd: C, 61.06; H, 5.49; N, 10.17. Found: C, 60.81; H, 5.50; N, 9.82.

General Procedure for the Bromination of Compounds 3, 5, and 7. To a solution of compounds **3**, **5**, or **7** (1 mmol) in $CHCl_3$ (20 mL) stirred at 0 °C under nitrogen atmosphere was added 4 equiv of NBS in $CHCl_3$. The stirring was continued in the dark until the reaction was complete as monitored by TLC. The reaction mixture was poured into water and extracted with dichloromethane. The organic phase was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The resulting crude product was purified by chromatography on silica gel by using CH_2Cl_2–petroleum ether (1/1) as eluant to give dibromo derivatives **8**, **9**, or **10**.

*2,2′-Bi(5-bromo-3-cyano-4-(2-ethylhexyloxy)thiophene) (**8**).* Yield: 60%. Yellow pale solid. Mp = 77–78 °C; this compound rapidly decomposes in the air. ^{1}H NMR ($CDCl_3$): δ 0.89–0.99 (m, 12H), 1.25–1.58 (m, 18H), 4.18 (d, 4H, ^3J = 5.4 Hz). ^{13}C NMR ($CDCl_3$): δ 11.1, 14.0, 22.9, 23.4, 29.0, 30.0, 40.1, 77.4, 99.9, 105.0, 112.2, 138.1, 155.5.

*2,5-Bis(5′-bromo-3′-cyano-4′-hexyloxy-2′-thienyl)thiophene (**9**).* Yield: 80%. Yellow pale solid. Mp = 90–92 °C. ^{1}H NMR ($CDCl_3$): δ 0.88–0.94 (m, 6H), 1.32–1.38 (m, 8H), 1.48–1.53 (m, 4H), 1.76–1.83 (m, 4H), 4.25 (t, 4H, ^3J = 6.6 Hz), 7.53 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 25.3, 29.8, 31.4, 75.2, 96.8, 102.3, 113.1, 127.8, 134.8, 142.6, 155.0. MS (MALDI-TOF): $C_{26}H_{28}Br_2N_2O_2S_3$ calcd 655.9 (M^+), found 655.6. Anal. Calcd: C, 47.57; H, 4.30; N 4,.27. Found: C, 47.56; H, 4.28; N, 4.21.

*4,7-Bis(5′-bromo-3′-cyano-4′-hexyloxy-2′-thienyl)benzo[c]-[1,2,5]thiadiazole (**10**).* Yield: 85%. Bright red solid. Mp = 70–71 °C. ^{1}H NMR ($CDCl_3$): δ 0.89–0.94 (m, 6H), 1.34–1.40 (m, 8H), 1.51–1.56 (m, 4H), 1.79–1.86 (m, 4H), 4.29 (t, 4H, ^3J = 6.6 Hz), 8.40 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.5, 25.3, 29.9, 31.4, 75.3, 101.5, 104.1, 113.5, 124.6, 127.3, 143.6, 151.6, 155.4. MS (MALDI-TOF): $C_{28}H_{28}Br_2N_4O_2S_3$ calcd 708.9 (M^+ + H), found 708.5. Anal. Calcd: C, 47.46; H, 3.98; N,7.91. Found: C, 47.23; H, 4.02; N, 7.71.

General Procedure for Stille Coupling Reaction with the Stannyl Derivative of Benzothienothiophene. Under argon atmosphere, 1.6 M *n*-BuLi in hexane (1.2 equiv) was added to a solution of benzothienothiophene (**11**) (1 equiv) in 50 mL of anhydrous THF at −10 °C. The mixture was stirred for 40 min, and 1.2 equiv of chlorotrimethylstannane was added dropwise. The temperature was slowly increased from −10 °C to room temperature and stirred for 12 h at room temperature. A saturated NaF solution (20 mL) was added, and then the mixture was filtered through a plug of Celite. The filtrate was extracted with dichloromethane and dried with $MgSO_4$. Evaporation of the solvent gave the stannylated compound **12** (almost pure by ^{1}H NMR) and was used without purification in following reaction. ^{1}H NMR ($CDCl_3$): δ 0.45 (s, 9H), 7.32–7.37 (m, 2H), 7.40 (s, 1H), 7.83–7.86 (m, 2H).

In an oven-dried Schlenk tube, a solution of the bromo derivative (1 mmol), the stannyl derivative (2.5 equiv), and the catalyst $Pd(PPh_3)_4$ (10% molar) in toluene (10 mL) was refluxed for 18 h under argon atmosphere. After completion of the reaction as checked by TLC, water was added to the mixture and extracted with dichloromethane. The organic phase was dried with $MgSO_4$ and evaporated under reduced pressure. The residue was purified by precipitation in MeOH and chromatography on silica gel with petroleum ether and dichloromethane (1/1) as eluant.

*2,2′-Bi(5-(benzothieno[3,2-b]2-thienyl)-3-cyano-4-hexyloxythiophene) (**BT1**).* Yield: 60%. Red solid. Mp = 210–212 °C. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 6H, ^3J = 7.2 Hz), 1.00 (t, 6H, ^3J = 7.5 Hz), 1.35–1.40 (m, 8H), 1.50–1.65 (m, 8H), 1.88–1.96 (m, 1H), 4.25 (d, 4H, ^3J = 5.4 Hz), 7.35–7.47 (m, 4H), 7.56 (s, 2H), 7.82–7.87 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 11.2, 14.1, 23.1, 23.5, 29.0, 30.1, 40.4, 78.1, 104.8, 113.4, 118.6, 121.1, 123.8, 123.9, 124.5, 125.1, 132.3, 133.6, 135.6, 135.9, 138.0, 142.8, 153.1. MS (MALDI-TOF): $C_{46}H_{44}N_2O_2S_6$ calcd 848.17 (M^+), found 848.0. HRMS: m/z_{cal} = 871.1625 [$M^{+\bullet}$ + Na], m/z_{mes} = 871.1618.

*2,5-Bis(5′-(benzothieno[3,2-b]2-thienyl)-3′-cyano-4′-hexyloxy-2′-thienyl)thiophene (**BT2**).* Yield: 54%. Purple solid. Mp = 204–206 °C.

^{1}H NMR ($CDCl_3$): δ 0.93 (t, 6H, ^3J = 7.2 Hz), 1.37−1.41 (m, 8H), 1.54−1.58 (m, 4H), 1.89−1.99 (m, 4H), 4.31 (t, 4H, ^3J = 6.9 Hz), 7.38 (s, 2H), 7.28−7.40 (m, 4H), 7.58 (s, 2H), 7.75−7.80 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 25.5, 30.2, 31.6, 75.3, 101.8, 114.1, 117.5, 121.0, 121.1, 123.9, 124.9, 127.7, 128.5, 132.3, 134.5, 135.0, 135.2, 137.9, 139.6, 142.8, 152.5. MS (MALDI-TOF): $C_{46}H_{38}N_2O_2S_7$ calcd 874.09 (M^+), found 873.9. HRMS: m/z_{cal} = 897.0871 [$M^{+\bullet}$ + Na], m/z_{mes} = 897.0867

*4,7-Bis(5′-(benzothieno[3,2-b]2-thienyl)-3′-cyano-4′-hexyloxy-2′-thieny)benzo[c][1,2,5]thia-diazole (**BT3**).* Yield: 42%. Blue solid. Mp = 214−218 °C. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 6H, ^3J = 7.2 Hz), 1.36−1.38 (m, 8H), 1.49−1.60 (m, 4H), 1.88−1.98 (m, 4H), 4.38 (t, 4H, ^3J = 6.9 Hz), 7.36−7.44 (m, 4H), 7.62 (s, 2H), 7.84 − 7.87 (m, 4H), 8.49 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 22.5, 25.3, 29.5, 31.4, 75.3, 104.1, 114.3, 117.6, 120.8, 120.9, 123.7, 124.4, 124.7, 125.2, 127.1, 132.1, 134.5, 135.3, 137.7, 140.6, 142.5, 151.7, 153.1. MS (MALDI-TOF): $C_{48}H_{38}N_4O_2S_7$ calcd 926.10 (M^+), found 925.9. HRMS: m/z_{cal} = 949.0932 [$M^{+\bullet}$ + Na], m/z_{mes} = 949.0929.

■ ASSOCIATED CONTENT

Supporting Information

X-ray data of compounds **5** and **7** (CIF), Figure.S1 and Figure.S2 presenting the stacking modes in the crystal structures of **5** and **7**, tables giving the atomic coordinates corresponding to the computational data of **BTn**, Figure S3 presenting the CV traces of compounds **BTn**, copies of ^{1}H and ^{13}C NMR of compounds **5**, **7−10**, **BT1**, **BT2** ,and **BT3**, and copies of MALDI-ToF spectra of compounds **BTn**. This material is available free of charge via the Internet at http://pubs.acs.org./.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pierre.frere@univ-angers.fr.

Notes

The authors declare no competing financial interest.

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