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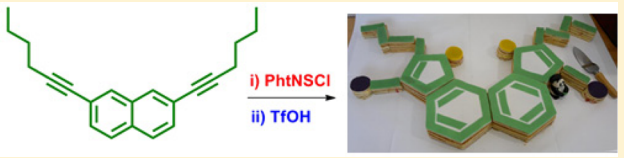
Regioselective Electrophilic Access to Naphtho[1,2-*b*:8,7-*b*′]- and -[1,2-*b*:5,6-*b*′]dithiophenes

Caterina Viglianisi,* Lucia Becucci, Cristina Faggi, Sara Piantini, Piero Procacci, and Stefano Menichetti*

Dipartimento di Chimica 'Ugo Schiff', Università di Firenze, Via della Lastruccia 3-13, I-50019 Sesto Fiorentino, Italy

Supporting Information

ABSTRACT: A two-step one purification access to dichloronaphtho[1,2-*b*:8,7-*b*′] and [1,2-*b*:5,6-*b*′]dithiophenes using bis-alkylnaphthyl alkynes and phthalimidesulfenyl chloride as starting materials has been developed. The functionalization of the carbon−chlorine bonds allowed further modification of NDT core, broadening the potential of the methodology.



Compounds containing the benzo[*b*]thiophene nucleus have found a huge number of applications in medicinal chemistry as well as, more recently, in material science. For example, raloxifene (**1**) (Figure 1) is a marketed drug used for

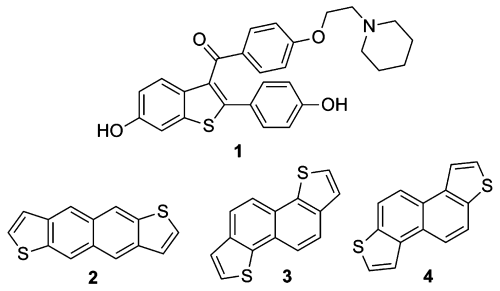


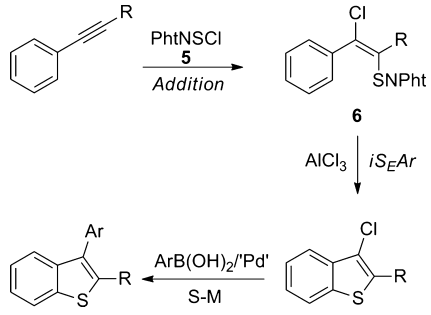
Figure 1. Raloxifene (**1**) and model naphthodithiophenes (NDTs) **2**–**4**.

osteoporosis and estrogen-related cancers;[1] several raloxifene analogues show a similar selective estrogen receptor modulator (SERM) activity,[2] and many other compounds containing the benzo[*b*]thiophene skeleton display a broad range of pharmacological effects.[3−7] On the other hand, thiophene and benzothiophene derivatives have recently found application in material science for the preparation of OLED and OFET.[8] Among these systems, polycondensed heteroaromatics like naphthodithiophenes (NDTs) **2**–**4** (Figure 1) are commonly indicated as useful cores for electronic organic devices yet scarcely studied mainly due to the difficulties of preparation.[9]

Hence, any new approach to the synthesis of the benzothiophene moiety represents an important achievement, and particularly appealing are those methods that allow the easy regioselective fusion of the five-membered ring to a polycondensed aromatic. Several modern and elegant methods foresee the cyclization of 1-thio-2-unsuturated substituted aromatics using stoichiometric or catalytic amounts of a proper promoter.[10]

Interestingly, in some examples the sulfur atom is directly inserted on the *ortho*-disubstituted aromatic while promoting the cyclization.[9,11] All these methods require the preventive regioselective bis-functionalization of an aromatic skeleton, generally not a trivial task above all when two thiophene units have to be assembled. Several years ago, we reported an easy synthesis of 3-chlorobenzo[*b*]thiophenes exploiting the reactivity of the phthalimidesulfenyl chloride (PhtNSCl, Pht = phthaloyl, **5**).[12] As described in Scheme 1, the procedure takes

Scheme 1. Synthesis of Benzo[*b*]thiophenes from Monoalkylarylalkynes via Electrophilic Addition and Internal Electrophilic Aromatic Substitution



advantage of the high stereo- and regioselective electrophilic addition of **5** to alkylaryl(or diaryl)alkynes that allowed the preparation of (*E*)-1-chloro-1-aryl-2-*N*-thiophthalimides **6**.[12,13]

These very stable crystalline sulfenamides can be cyclized to 3-chlorobenzo[*b*]thiophenes using a Lewis acid that, probably interacting with the phthalimide nitrogen (vide infra), enhances the electrophilic character of the sulfenic sulfur allowing an intramolecular electrophilic substitution (iS_EAr). The procedure has been recently optimized, demonstrating its applicability on solid phase and its utility for the preparation of raloxifene analogues using, as an additional final step, the 3-chloro-substituted carbon of benzo[*b*]thiophene as a supplementary functionalization opportunity in Suzuki−Miyaura (S−

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M) or other Pd-catalyzed cross-coupling reactions (Scheme 1).[14]

Obviously, this methodology does not require an *ortho*-functionalized aromatic system. Thus, it seems particularly feasible for the preparation of polycondensed systems like NDTs **2**−**4** using bis-alkylnaphthyl alkynes as starting materials. These latter, in turn, can be easily prepared via a double-Sonogashira cross-coupling method. Indeed, applying the Sonogashira reaction to 2,7-, 2,6-, and 1,5-bis-naphtho-*O*-triflates, we prepared and used bis-naphthoalkynes **7**−**10**, depicted in Figure 2, to verify the applicability of the above-mentioned procedure for the preparation of NDT derivatives.

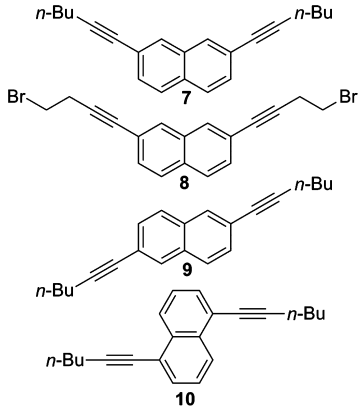
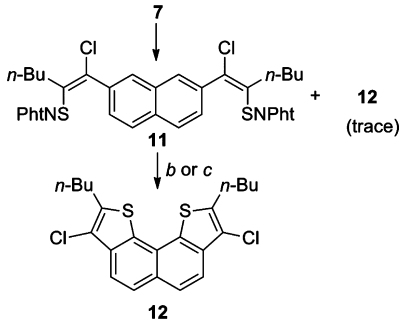


Figure 2. Bis-naphthoalkynes **7**−**10** used in this study.

Compound **7** was reacted with **5** in dry DCM at room temperature for 12 h to give the expected bis-*N*-vinyl-thiophthalimide **11** in quite good yield (Scheme 2). The crude was separated in two identical portions; the first was purified by flash chromatography (67% yield of **11**) and reacted with $AlCl_3$ in dry DCM while the second was reacted with $AlCl_3$ under the same conditions without any previous purification. Satisfied, we verified the formation of 2,9-dibutyl-3,8-dichloronaphtho[1,2-*b*:8,7-*b*′]dithiophenes (**12**) as a single regioisomer isolated, in both experiments, in reasonable and comparable yields (52% and 48%, respectively), indicating the possibility to use this procedure to access to NDT systems also avoiding the column chromatography purification of the intermediate *N*-thiophthalimides (Scheme 2).

Scheme 2[a]



[a]Reagents and conditions: (a) **5**, 2.2 equiv of DCM, rt, 12 h, 67%; (b) $AlCl_3$, 4 equiv, DCM, rt, 30 min, 48%; (c) TfOH, 4 equiv of DCE, 60 °C, 17 h, 65%.

Actually, a detailed examination of the ^1H NMR of the crude obtained after the reaction of **5** with **7** showed the formation of tiny amounts of naphthodithiophene **12** directly during the electrophilic addition step. We speculate that, as it occurred in the related iS_EAr of *o*-diarylamino-*N*-thiophthalimides leading to [1,4]benzothiazine heterocyles,[15] HCl, reasonably formed during the addition process by reaction of sulfenyl chloride **5** with adventitious traces of water, could also operate as promoter of the iS_EAr process. In order to verify this hypothesis, we kept *N*-thiophthalimide **11** in dry DCM previously saturated with gaseous HCl, and indeed, we could observe the formation of reasonable amounts of **12** without, however, achieving the complete consumption of the starting material. Enduring to study the ability of protic acids in promoting the iS_EAr, eventually we were able to isolate quite good yield of **12** (65%) reacting crude **11** with 4 equiv of triflic acid in dichloroethane (DCE) at 60 °C (Scheme 2).

Additional information on the actual mechanism of this acid-promoted (Lewis and/or protic) thiophene ring closure from (*E*)-1-chloro-1-aryl-2-*N*-thiophthalimides was collected by reacting **11** and $AlCl_3$ in the presence of stoichiometric amounts of 2,6-ditert-butylpyridine, a hindered base able to trap protons but unable to coordinate $AlCl_3$. Interestingly, under these conditions, only trace amounts of **12** were observed in the crude reaction mixture, suggesting that the protonation of the sulfenamide nitrogen,[16] more than the interaction with the Lewis acid, is the real trigger event for the cyclization. Thus, in this case,[17] probably, protons are the real promoters of the iS_EAr, and $AlCl_3$, or the other Lewis acids able to provide the cyclization,[12] serve just to generate protons in the reaction mixture as it occurs in several other peculiar examples recently reported by Spencer.[18]

The use of triflic acid as promoter, avoiding the formation of the aluminum salts during the alkaline workup, further simplifies the synthetic procedure, and we operated as depicted in Scheme 2 to cyclize the crude *N*-thiophthalimides obtained by addition of **5** to alkynes **8** and **9** (see the Experimental Section). Under these conditions, bis-naphthodithiophenes **13** and **14** were isolated, from the corresponding crude *N*-thiophthalimides as single regioisomers in 78% and 85% yields respectively (Figure 3). On the other hand, the electrophilic addition of **5** to 1,5-bis-alkyne **10** gave the worst results, and the following cyclization, using either TfOH or $AlCl_3$, afforded moderate yields (42%) of an inseparable 1:1 mixture of NDT **15** and compound **16** containing a thiophene and a six-membered thiapyrene ring (Figure 3).

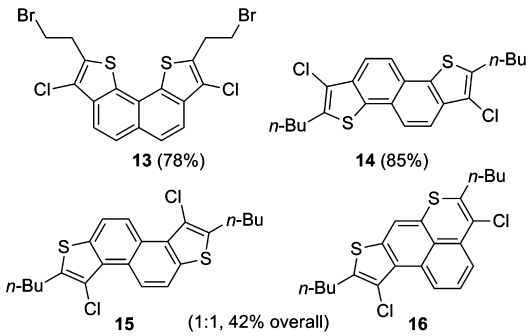


Figure 3. NDTs **13**−**15** and mixed thiophene/thiapyrene derivative **16** prepared in this study.

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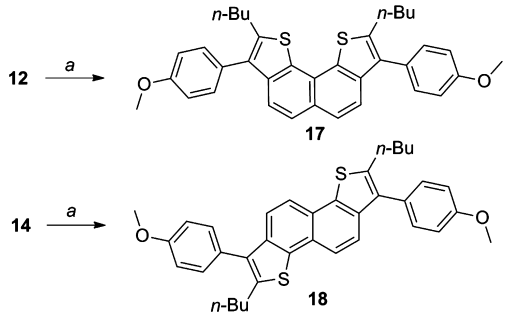
The results obtained show that the transformation of alkylarylalkynes into 3-chlorobenzothiophene, mediated by sulfenyl chloride **5**, can be easily applied for the preparation of NDT derivatives, in particular using 2,6- and 2,7-dialkynyl-substituted naphthalenes as starting material.

Worthy of mention is the possibility to easily isolate the quite uncommon [1,2-*b*:8,7-*b*′]dithiophene derivatives like **12** and **13**, the former testifying how the proposed procedure is also perfectly tolerated by the primary bromide group. Compounds **12**−**14** were isolated as single regioisomers as expected due to the high nucleophilicity of the α-position of the naphthalene ring. Indeed, in the case of *N*-thiophthalimide obtained by addition of sulfenyl chloride **5** to 1,5-bis-substituted alkynyl-naphthalene **10**, the high reactivity of α position induces a certain amount of "1 to 8" ring closure (roughly 1/4 of the cyclization processes) leading to the formation of derivative **16** containing a thiophene and a thiapyrene ring system. At the same time, the high reactivity of the naphthalene α-position does not allow the use of the present method to prepare compound **2** (Figure 1) and its syn-isomer, naphtho[2,3-*b*:7,6-*b*′]dithiophene.

The above procedure leads to the formation of 3-chloro-2-alkyl-substituted naphthothiophenes. Although α-unsubstituted NDTs are the most useful materials for further application to materials science and "naked" NDTs cannot be prepared with this method, the presence of the chlorine atom, instead of being a drawback, can be exploited as an additional synthetic option. In fact, the carbon−chlorine bond allows the functionalization of the heteroaromatic ring via cross-coupling reactions.[14] For example, DBTs **12** and **14** were reacted with *p*-methoxyboronic acid using PEPSSI-*i*-Pr as catalyst under S−M cross-coupling conditions to give bis-aryl derivatives **17** and **18** in 66%[19] and 89% yield, respectively, as reported in Scheme 3.

Scheme 3[a]



[a]Reagents and conditions: (a) *p*-methoxyphenylboric acid (3 equiv), K_2CO_3 (2 equiv), PEPSSI-*i*Pr (0.1 equiv), toluene, 100 °C, 17−40 h.

This reaction is of particular interest considering that metal-catalyzed cross-coupling processes are often used as the method of choice for the functionalization or the polymerization steps required for transforming thiophene-containing derivatives into materials useful for electronic organic devices. Hence, the procedure described in this paper offers an easy way to obtain NDT derivatives, like **12**−**14**, prearmed for a cross-coupling-based structural modification.

Polycondensed systems **12**−**18** were fully characterized, and in the case of NDTs **12**, **14**, **15**,[20] **17**, and **18**, suitable crystals for X-ray analysis were obtained, confirming structural attributions.

The solid-state packaging of **12** is quite peculiar: the NDT units are superimposed at 3.51 Å with an alternate little deviation from the molecular axis that prevents a full eclipsing. A columnar structure appears in the crystal with one alkyl group completely out of the plane of the dithiophene skeleton. Interestingly, the direction of the sulfur atoms (i.e., the convexity of structure **12**) is inverted in adjacent rows of such a "columnar" network. On the other hand, compounds **14** and **15** are completely flat, all non-hydrogen atoms, including all sp3 carbons, laying exactly on a plane, giving rise to a tridimensional structure of parallel layers with a different packaging motif at a distance of 3.52 and 3.56 Å, respectively. In particular, in the solid state, NDT **14** shows a network of short contacts (2.77 Å) between a hydrogen of the CH_2 linked to the 2-thienyl position and the π-electronic density in the average plane of molecules of the upper and lower layers (see Figure *SI_06* in the Supporting Information).

Density functional calculations (Experimental Section) were employed to compute the optimized geometry for each of the compounds **12**, **14**, **17**, and **18** in the gas phase. Expectedly, for all molecules, the HOMO−LUMO orbitals are systematically delocalized on the extended planar aromatic system. HOMO−LUMO energy gaps, reported in Table 1, appear slightly

Table 1. HOMO and LUMO Energies[a] for NDTs 12, 14, 17, and 18

NDT	HOMO (eV)	LUMO (eV)	ΔE (eV)
12	−5.76038	−1.18451	4.57587
14	−5.61752	−1.32737	4.29015
17	−5.05207	−0.89634	4.15572
18	−5.13778	−0.91403	4.22375

[a]Calculated at DFT B3LYP-6-31G* level.

sensitive either to the shape of the NDT skeleton or to the substituent on C3 (i.e., a chlorine or a *p*-methoxybenzene). Interestingly, in compounds **17** and **18**, the additional aromatic substituents on C3 appear to contribute only marginally to the HOMO−LUMO orbitals and, correspondingly, to the narrowing of the energy gap. In these compounds, the *p*-methoxybenzene moieties are in a tilted, quasi-T-shaped configuration with respect to the NTD skeleton, an effect very likely due to steric hindrance, that is maintained in the crystal phase (HOMO−LUMO orbitals and ORTEP diagrams of **12**, **14**, **17**, and **18** are available as Supporting Information).

The computed band gaps listed in Table 1, confirmed by UV−vis spectra (see the Supporting Information), are in agreement with those reported for similar structures[9] and indicate that after suitable structural transformations, such as polymerization or introduction of push−pull termini, the NDTs prepared in this study can reach the HOMO−LUMO gaps required for application in organic electronic devices.

In summary, a simple access to NDT systems, including uncommon naphtho[1,2-*b*:8,7-*b*′]dithiophenes, has been achieved using easily available bis-alkylarylalkynes and sulfenyl chloride **5** as starting materials. The procedure foresees two electrophilic processes and required a single purification. The possibility to use the carbon−chlorine bond to further functionalize the NDT core enlarges the scope of this methodology for the preparation of polyconjugated heteroacenes with applications in organic electronic devices.

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EXPERIMENTAL SECTION

General Experimental Methods. Commercially available reagents, catalysts, and ligands were used as obtained, unless otherwise stated, from freshly opened containers without further purifications. Toluene was distilled from sodium, THF was distilled from sodium in the presence of the blue color of benzophenone kethyl, and DCM and dichloroethane (DCE) were distilled from $CaCl_2$. All of the reactions are monitored by TLC on commercially available precoated plates (silica gel 60 F 254), and the products were visualized with acidic vanillin solution. Silica gel 60, 230−400 mesh, is used for column chromatography. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded, unless otherwise noted, in $CDCl_3$ at 400 and 100 MHz using residual $CHCl_3$ at 7.26 ppm and CDCl3 at 77.00 ppm as reference lines, respectively. FTIR spectra are recorded in $CDCl_3$ solutions. UV−vis spectra are recorded in dry DCM using 10^{-4} M solutions. Cyclic voltammograms were obtained on a platinum working electrode by scanning the applied potential between −0.45 and +1.250 V vs the $Fc^+/0$ couple, at a scan rate of 200 mVs^{-1}, in a DCM solution of 0.2 M tetrabutylammonium hexafluorophosphate and 5×10^{-4} M of the different NDTs. **Ab initio calculations.** Hydrogen atoms were added to the coordinates of the heavy atoms (taken from the raw crystallographic data) by means of the program ORAC.[21] These starting coordinates underwent a molecular-mechanics minimization using the AMBER/GAFF force field.[22] On the resulting coordinates, a full ab initio geometry optimization was performed at the Hartree−Fock level of theory using a 4-31G basis set. The last configuration, optimized at the HF/4-31G level, underwent a further geometry refinement through a constrained optimization using density functional theory (DFT) with the B3-LYP exchange-correlation functional[23,24] and the split-valence polarized basis-set 6-31G(d). The DFT-constrained optimization involved only the atoms belonging to the extended NTD aromatic system including (in **17** and **18**) the *p*-methoxybenzene substituents (alkyl groups were kept frozen). The HOMO−LUMO energy gap was computed using the eigenvalues of the last optimized configuration at the B3-LYP/6-31G(d) level of theory. All ab initio calculations were done with the program Gaussian09. The HOMO and LUMO orbitals surfaces for the resulting minimized structures were produced using the cross-platform molecule editor Avogadro.[25] **X-ray.** Measurements and X-ray analysis were carried out at 100 K for compounds **12** and **14** and at 120 K for compounds **15**, **17**, and **18**. Cu/Kα radiation (40 mA/−40 kV), monochromated was used for cell parameter determination and data collection. The integrated intensities, measured using the ω scan mode, were corrected for Lorentz and polarization effects.[26] Direct methods of SIR2004[27] were used in solving the structures, and they were refined using the full-matrix least-squares on *F*2 provided by SHELXL97.[28] A multiscan symmetry-related measurement was used as the experimental absorption correction type. Hydrogen atoms were all assigned in calculated positions for compounds **12**, **15**, and **18**, whereas for compounds **14** and **17** they were found, when possible, in the Fourier difference map. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as isotropic. The X-ray CIF files are available as Supporting Information and have been deposited at the Cambridge Crystallographic Data Centre and allocated with the deposition numbers CCDC 912636 (compound **12**), CCDC 912635 (compound **14**), CCDC 912638 (compound **15**), CCDC 912637(compound **17**) and CCDC 912639 (compound **18**). Copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk; Internet://www.ccdc.cam.ac.uk).

Synthesis. Bis-alkynes **7**−**10** were prepared from the corresponding 2,7-, 2,6, and 1,5-bis-*O*-triflates using standard Sonogashira cross coupling conditions. The preparation of **7** is reported as an example of the general procedure.

*2,7-Di(hex-1-yn-1-yl)naphthalene (**7**).* In a Schlenk tube under nitrogen, naphthalene-2,7-diyl-bis(trifluoromethansulfonate) (200 mg; 0.47 mmol), CuI (12 mg; 0.06 mmol) ,and $Pd(PPh_3)_2Cl_2$ (46 mg; 0.07 mmol) were suspended in dry DMF (1.6 mL). *N*,*N*-Diisopropylethylamine (364 mg; 2.82 mmol) and a solution of 1-hexyne (115 mg; 1.41 mmol) in THF dry (1.6 mL) were added to the suspension at rt, and the mixture was stirred at 100 °C for 19 h. The mixture was then diluted with petroleum ether (100 mL) and the organic phase washed with saturated NH_4Cl (1 × 100 mL) and water (2 × 100 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a brown oil (270 mg). The crude was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 1/5) to give bis-alkyne **7** as a colorless oil (120 mg; 96% yield). ^1H NMR δ: 7.81 (s, 2H); 7.68 (d, *J* = 8.8 Hz, 2H); 7.41 (dd, *J* = 8.8 and 1.6 Hz; 2H); 2.46 (t, *J* = 6.8 Hz, 4H); 1.74−1.41 (m, 8H); 0.97 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR δ: 132.7; 131.4; 130.5; 129.1; 127.5; 122.0; 91.2; 80.7; 30.8; 22.1; 19.2; 13.6 ppm. IR ν: 3064 (C−H st aromatic); 2963 + 2932 (C−H st aliphatic); 2240 (C≡C st) cm^{-1}. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.23; H, 8.51

*2,7-Bis(4-bromobut-1-yn-1-yl)naphthalene (**8**).* Following the general procedure the crude was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 4/1) to give bis-alkyne **8** as a colorless oil (140 mg, 37%). ^1H NMR δ: 7.85 (s, 2H); 7.71 (d, *J* = 8.4 Hz, 2H); 7.45 (dd, *J* = 8.4 and 1.4 Hz; 2H); 3.56 (t, *J* = 7.2 Hz, 4H); 3.03 (t, *J* = 7.2 Hz, 4H) ppm. ^{13}C NMR δ: 132.5; 131.9; 131.0 ; 129.2; 127.8; 121.2; 87.4; 82.5;29.5; 24.0 ppm. IR ν: 3066 (C−H st aromatic); 2972 + 2925 (C−H st aliphatic); 2247 (C≡C st) cm^{-1}. Anal. Calcd for $C_{22}H_{14}Br_2$: C, 55.42; H, 3.62. Found: C, 55.55; H, 3.27.

*2,6-Di(hex-1-yn-1-yl)naphthalene (**9**).* Following the general procedure, the crude was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 1/3) to give **9** as a pale yellow solid (200 mg, 57% yield).Mp: 77−78 °C. ^1H NMR δ: 7.86 (as, 2H); 7.68 (d, *J* = 8.4 Hz, 2H); 7.45 (dd, *J* = 8.4 and 1.6 Hz; 2H); 2.47 (t, *J* = 7.2 Hz, 4H); 1.68−1.60 (m, 4H); 1.58−1.48 (m, 4H); 1.01 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR δ: 132.1; 130.7; 129.3; 127.4; 121.8; 91.3; 80.8; 30.9; 22.1; 19.2; 13.6 ppm. IR ν: 3060 (C−H st aromatic); 2965 + 2931 (C−H st aliphatic); 2241 (C≡C st) cm^{-1}. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.41; H, 8.44.

*1,5-Di(hex-1-yn-1-yl)naphthalene (**10**).* Following the general procedure the crude is purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 1/5) to give bis-alkyne **10** as a yellow solid (265 mg, 83%). Mp: 54−55 °C. ^1H NMR δ: 8.31 (dd, *J* = 8.2 and 0.8 Hz, 2H); 7.65 (dd, *J* = 7.0 and 0.8 Hz, 2H); 7.47 (dd, *J* = 8.2 and 7.0 Hz, 2H); 2.58 (t, *J* = 7.0 Hz, 4H); 1.74−1.67 (m, 4H); 1.62−1.53 (m, 4H); 1.01 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR δ: 133.4; 130.4; 126.2; 125.7; 122.1; 95.7; 78.5; 30.9; 22.1; 19.4; 13.6 ppm. IR ν: 3056 (C−H st aromatic); 2961 + 2926 + 2875 (C−H st aliphatic); 2245 (C≡C st) cm^{-1}. Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.77; H, 8.19.

The addition of phthalimidesulfenyl chloride **5** to alkynes **7**−**10** was carried out following previously reported procedures.[12,14] The preparation of *N*-thiophthalimide **11** is described as an example of the general protocol. *N*-Thiophthalimides obtained reacting **5** with alkynes **8**−**10** were similarly obtained and used after workup without further purifications.

*N-Thiophthalimide (**11**).* To a solution of alkyne **7** (293 mg, 1.02 mmol) in dry DCM (10 mL) was added dropwise a solution of sulfenyl chloride **5** (485 mg, 2.23 mmol) in dry DCM (22 mL) at −10 °C under nitrogen during 1 h. The mixture was stirred at rt for 12 h and then diluted with DCM (30 mL) and washed with water (2 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a brownish solid (780 mg). Half of this crude (390 mg) was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 2/1) to give *N*-thiophthalimide (**11**) as a white solid (140 mg, 67%). Mp: 151−152 °C. ^1H NMR δ: 7.90 (as, 2H); 7.83−7.77 (m, 4H); 7.74−7.67 (m, 6H); 7.65 (dd, *J* = 8.4 and 1.6 Hz, 2H); 2.44 (t, *J* = 8.4 Hz, 4H); 1.80−1.72 (m, 4H); 1.45−1.36 (m, 4H); 0.93 (t, *J* = 8.4 Hz, 6H) ppm. ^{13}C NMR δ: 167.4; 135.6; 134.8; 134.6; 132.8; 131.8; 131.6; 129.6; 128.4; 127.9; 127.3; 123.8; 32.1; 29.6; 22.5; 13.8 ppm. IR ν: 2965 (C−H st aliphatic); 1784 + 1741 + 1711 (C=O st Pht) cm^{-1}. Anal. Calcd for $C_{38}H_{32}Cl_2N_2O_4S_2$: C, 63.77; N, 3.91; H, 4.51. Found: C, 63.63; N, 4.00; H, 4.77.

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Cyclization of crude *N*-thiophthalimides to the corresponding NDTs was carried out using CF_3SO_3H or (and) $AlCl_3$. Both experimental conditions are reported for the preparation of derivative **12**. The procedure with triflic acid is the general protocol used to obtain the other NDTs.

*2,9-Dibutyl-3,8-dichloronaphtho[1,2-b:8,7-b′]dithiophene (**12**). (a). With $AlCl_3$.* To a solution of **11** (309 mg; 0.43 mmol) in dry DCM (20 mL) kept under nitrogen was added $AlCl_3$ (230 mg; 1.73 mmol) in small portions. A dark violet suspension was formed immediately. The mixture was stirred for 30 min at rt and diluted with DCM (30 mL), and the organic phase was washed with 1 M NaOH (3 × 30 mL) and water (4 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a crude (150 mg) purified by flash chromatography on silica gel (eluent: petroleum ether) to give NDT **12** as a white solid (94 mg, 52%).

(b). With CF_3SO_3. A vial containing a solution of **11** (150 mg; 0.21 mmol) and CF_3SO_3H (126 mg; 0.84 mmol) in DCE (23 mL) was stirred at 60 °C for 17 h. The mixture was diluted with DCM (20 mL) and the organic phase washed with saturated Na_2CO_3 (2 × 30 mL) and water (4 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a brown solid (80 mg) that was purified by flash chromatography on silica gel (eluent: petroleum ether) to give **12** as white solid (58 mg, 65%). Mp: 91−92 °C. ^{1}H NMR δ: 7.92 (d, J = 8.6 Hz, 2H); 7.86 (d, J = 8.6 Hz, 2H); 3.09 (t, J = 7.6 Hz, 4H); 1.88−1.81 (m, 4H); 1.56−1.47 (m, 4H); 1.02 (t, J = 7.6 Hz, 6H) ppm. ^{13}C NMR δ: 139.7; 135.0; 130.4; 129.5; 126.3; 123.5; 119.3; 118.7; 32.7; 28.2; 22.3; 13.8 ppm. MS m/z (int rel) 420 (56 $M^{\bullet+}$): 377 (100); 336 (54). Anal. Calcd for $C_{22}H_{22}Cl_2S_2$: C, 62.70; H, 5.26. Found: C, 62.62; H, 5.01. X-ray: orthorhombic, space group *Pcca*, a = 22.857(1) Å, b = 7.330(1) Å, c = 23.337(1) Å, V = 3909.9(6) Å^3, Z = 8, D_c = 1.432, μ = 4.995 mm^{-1}, F(000) = 1760. 11144 reflections were collected with a 4.25 < θ < 71.53 range with a completeness to θ 96.0%; 3661 were unique, the parameters were 236 and the final R index was 0.0565 for reflections having $I > 2\sigma I$ and 0.0753 for all data. No significant intra- or intermolecular interactions, such as H-bonds or π-stacking between aromatic rings, were detected.

*2,9-Bis(2-bromoethyl)-3,8-dichloronaphtho[1,2-b:8,7-b′]dithiophene (**13**).* The crude obtained following the general procedure is purified by flash chromatography on silica gel (eluent: petroleum eter/DCM = 1/1) to give the NDT **13** as a brown solid (61 mg, 78% yield). Mp: 154−155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J = 9.0 Hz, 2H); 7.90 (d, J = 9.0 Hz, 2H); 3.74 (t, J = 6.0 Hz, 4H); 3.64 (t, J = 6.0 Hz, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9; 134.8; 130.9; 130.1; 126.7; 12.3; 120.5; 119.8; 31.8; 30.2 ppm. MS m/z (int rel %) 526/524/522/520 (35/81/76/28, $M^{\bullet+}$); 431/429/427 (50/100/51); 347/349 (30). Anal. Calcd for $C_{18}H_{12}Br_2Cl_2S_2$: C, 41.33; H, 2.31. Found: C, 41.11; H, 2.16.

*2,7-Dibutyl-1,6-dichloronaphtho[1,2-b;5,6-b′]dithiophene (**14**).* The crude obtained following the general procedure is purified by flash chromatography on silica gel (eluent: petroleum ether/DCM = 4/1) to give NDT **14** as a white solid (81 mg, 85%). Mp: 127−128 °C. ^{1}H NMR δ: 7.92 (d, J = 8.4 Hz, 2H); 7.82 (d, J = 8.4 Hz, 2H); 3.01 (t, J = 7.6 Hz, 4H); 1.82−1.74 (m, 4H); 1.53−1.44 (m, 4H); 1.0 (t, J = 7.6 Hz, 6H) ppm. ^{13}C NMR δ: 138.2; 134.9; 134.5; 125.7; 120.6; 120.5; 118.5; 32.6; 28.0; 22.3; 13.8 ppm. MS m/z (int rel %) 420 (56 $M^{\bullet+}$); 377 (100); 336 (54). Anal. Calcd for $C_{22}H_{22}Cl_2S_2$: C, 62.70; H, 5.26. Found: C, 62.58; H, 5.32. X-ray: triclinic, space group *P*-1, a = 6.946(1) Å, b = 7.720(1) Å, c = 9.057(1) Å, α = 90.861(6), β = 89.656(6), γ = 98.724(5)°, V = 479.9(1) Å^3, Z = 2, D_c = 1.458, μ = 5.086 mm^{-1}, F(000) = 220. 2478 reflections were collected with a 6.45 < θ < 61.76 range with a completeness to θ 96.6%; 1442 were unique, the parameters were 154 and the final R index was 0.0273 for reflections having $I > 2\sigma I$ and 0.0313 for all data. In the asymmetric unit there is a half molecule; this is because the center of symmetry in the molecule coincides with the inversion center (group *P*-1).

*2,7-Dibutyl-1,6-dichloronaphtho[1,2-b;5,6-b′]dithiophene (**15**) and 5,9-Dibutyl-4,10-dichlorobenzo[de]thieno[3,2-g]thiochromene (**16**).* The crude obtained following the general procedure was purified by flash chromatography on silica gel (eluent: petroleum ether) to give a 1:1 mixture of **15** and **16** as a pale yellow glassy solid (63 mg, 42%). ^{1}H NMR δ: 9.54 (d, J = 9.0 Hz, 2H, **15**), 9.20 (dd, J = 8.0 and 1.2 Hz, 1H, **16**), 7.90 (d, J = 9.0 Hz, 2H, **15**), 7.72 (dd, J = 7.5 and 1.2 Hz, 1H, **16**), 7.45 (dd, J = 8.0 and 7.5 Hz, 1H, **16**), 7.33 (s, 1H, **16**), 3.05 (t, J = 7.5 Hz, 4H, **15**), 2.94 (t, J = 7.5 Hz, 2H, **16**), 2.54 (t, J = 7.8 Hz, 2H, **16**), 1.82−1.44 (m, 16H **15** + **16**), 1.03−0.83 (m, 12H **15** + **16**) ppm. ^{13}C NMR δ: 139.6; 131.8; 127.6; 127.2; 122.2; 121.1; 120.3; 1198; 113.1; 34.8; 32.3; 32.2; 29.8; 28.5; 28.3; 22.4; 22.3; 22.2; 13.8; 13.7 ppm. Anal. Calcd for $C_{22}H_{22}Cl_2S_2$ (on the mixture): C, 62.70; H, 5.26. Found: C, 62.28; H, 5.04. A slow evaporation of a DCM solution of a 1:1 mixture of **15** and **16** allowed the manual selection of colorless plate of pure NDT **15**, suitable for X-ray analysis, formed over a dark yellow gummy oil still containing both derivatives. X-ray: triclinic, space group *P*-1, a = 5.291(1) Å, b = 7.714(1) Å, c = 12.239(1) Å, α = 99.618(7)°, β = 94.426(7)°, γ = 102.384(8)°, V = 477.7(1) Å^3, Z = 2, D_c = 1.465, μ = 5.110 mm^{-1}, F(000) = 220. 3252 reflections were collected with a 5.98 < θ < 70.34 range with a completeness to θ 93.8%; 1722 were unique, the parameters were 118 and the final R index was 0.0406 for reflections having $I > 2\sigma I$ and 0.0573 for all data. Also in this case only a half molecule is contained in the asymmetric unit for the same reason as for compound **14**.

*2,9-Dibutyl-3,8-bis(4-methoxyphenyl)naphtho[1,2-b;8,7-b′]-dithiophene (**17**).* In a Schlenk tube under nitrogen to a mixture of *p*-methoxyphenylboronic acid (51 mg; 0.34 mmol), dry K_2CO_3 (94 mg; 0.68 mmol), and PEPPSI-*i*-Pr (3 mg; 0.04 mmol) was added a solution of NDT **12** (48 mg; 0.11 mmol) in dry toluene (1.5 mL). The mixture was stirred at 100 °C under an inert atmosphere for 17 h. The mixture was then diluted with diethyl ether (40 mL) and the organic phase washed with brine (3 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a brown oil (130 mg). The crude was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 1/4) to give derivative **17** as a white solid (42 mg, 66%) along with the monoarylated derivative **mono-17** (white solid, 7 mg, 11%). Mp: 89−90 °C. ^{1}H NMR δ: 7.83 (d, J = 8.4 Hz, 2H); 7.60 (d, J = 8.4 Hz, 2H); 7.38 (dd, J = 6.4 and 2.0 Hz, 4H); 7.07 (dd,, J = 6.4 and 2.0 Hz, 4H); 3.92 (s, 6H); 3.02 (t, J = 7.2 Hz, 4H); 1.86−1.81 (m, 4H); 1.48−1.38 (m, 4H); 0.92 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR δ: 158.9; 149.1; 143.0; 138.3; 134.4; 132.1; 131.4; 128.7; 127.9; 125.4; 120.5; 113.9; 55.3; 34.3; 28.7; 22.4; 13.8 ppm. MS m/z (int rel) 564 (100 $M^{\bullet+}$); 521 (38); 464 (28). Anal. Calcd for $C_{36}H_{36}O_2S_2$: C, 76.56; H, 6.42. Found: C, 76,44, H, 6.38. X-ray: triclinic, space group *P*-1, a = 9.525(1) Å, b = 11.520(1) Å, c = 13.591(1) Å, α = 81.463(4)°, β = 87.681(5)°, γ = 84.909(5)°, V = 1468.4(2) Å^3, Z = 2, D_c = 1.277, μ = 1.881 mm^{-1}, F(000) = 600. 16531 reflections were collected with a 4.66 < θ < 72.16 range with a completeness to theta 96.9%; 5625 were unique, the parameters were 473 and the final R index was 0.0464 for reflections having $I > 2\sigma$ I and 0.0772 for all data. No significant intra or intermolecular interactions were detected.

*2,9-Dibutyl-3-chloro-8-(4-methoxyphenyl)naphtho[1,2-b:8,7-b′]-dithiophene (**mono-17**).* ^{1}H NMR δ: 7.97 (d, J = 8.7 Hz, 1H); 7.91 (d, J = 8.4 Hz, 1H); 7.86 (d, J = 8.7 Hz, 1H); 7.63 (d, J = 8.4 Hz, 1H); 7.37 (d, J = 9.0 Hz, 2H); 7.07 (d, J = 9.0 Hz, 2H); 3.91 (s, 3H); 3.13 (t, J = 7.2 Hz, 2H); 3.01 (t, J = 7.2 Hz, 2H); 1.93−1.76 (m, 4H); 1.56−1.35 (m, 4H); 1.05 (t, J = 8.4 Hz, 3H); 0.92 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR δ: 159.0; 143.3; 139.5; 138.7; 134.8; 134.4; 131.7; 131.4; 130.9; 129.2; 127.7; 126.3; 125.6; 123.9; 121.1; 118.8; 118.7; 114.0; 55.3; 34.3; 32.7; 28.7; 28.2; 22.4; 22.4; 13.8 ppm. MS m/z (int rel) 492 (87, $M^{\bullet+}$); 449 (100); 203 (29). Anal. Calcd for $C_{29}H_{29}ClOS_2$: C, 70.63; H, 5.93. Found: C, 70.38; H, 6.01.

*2,7-Dibutyl-1,6-bis(4-methoxyphenyl)naphtho[1,2-b;5,6-b′]-dithiophene (**18**).* In a Schlenk tube under nitrogen to a mixture of *p*-methoxyphenylboronic acid (75 mg; 0. 49 mmol), dry K_2CO_3 (132 mg; 0.96 mmol), and PEPPSI-*i*-Pr (4 mg; 0.05 mmol) was added a solution of NDT **14** (70 mg; 0.16 mmol) in dry toluene (2 mL). The mixture was stirred at 100 °C under an inert atmosphere for 40 h. The mixture was then diluted with diethyl ether (40 mL) and the organic phase washed with brine (3 × 30 mL). The organic phase was dried over Na_2SO_4, filtered, and evaporated under vacuum to give a brown solid (130 mg). The crude was purified by flash chromatography on silica gel (eluent: DCM/petroleum ether = 1/3) to give derivative **18**

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as a white solid (80 mg, 89%). Mp: 171−172 °C. ^{1}H NMR δ: 7.92 (d, J = 8.4 Hz, 2H); 7.56 (d, J = 8.4 Hz, 2H); 7.36 (d, J = 8.7 Hz, 4H); 7.06 (d, J = 8.7 Hz, 4H); 3.91 (s, 6H); 2.91 (t, J = 7.2 Hz, 4H); 1.78−1.67 (m, 4H); 1.42−1.18 (m, 4H); 0.86 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR δ: 158.9; 141.1; 137.7; 136.2; 134.7; 131.2; 127.9; 125.7; 121.8; 120.8; 114.0; 55.3; 34.1; 25.6; 22.3; 13.8 ppm. MS m/z (int rel) 564 (100 $M^{\bullet+}$); 521 (43); 464 (28). Anal. Calcd for $C_{36}H_{36}O_2S_2$: C, 76.56; H, 6.42. Found: C, 76,39, H, 6.63. X-ray: triclinic, space group P-1, a = 10.689(1) Å, b = 14.404(1) Å, c = 19.076(1) Å, α = 98.344(3)°, β = 90.870(3)°, γ = 91.061(3)°, V = 2905.0(4) Å^3, Z = 2, D_c = 1.291, μ = 1.901 mm^{-1}, F(000) = 1200. 23272 reflections were collected with a 4.14 < θ < 70.66 range with a completeness to θ 95.3%; 10632 were unique, the parameters were 721 and the final R index was 0.0505 for reflections having $I > 2\sigma I$ and 0.0757 for all data. The asymmetric unit contains two independent molecules as they are not equivalent from a crystallographic point of view. It is mainly due to the different torsion angles between sulfur atoms and the alkylic chains. No significant intra- or intermolecular interactions can be detected.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of compounds **7**−**18**; CIF files and ORTEP diagrams of compounds **12**, **14**, **15**, **17**, and **18**; UV−vis spectra and cyclic voltammograms of compounds **12**−**14**, **17**, and **18**; HOMO−LUMO orbitals, atom coordinates, and absolute energies of compounds **12**, **14**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: caterina.viglianisi@unifi.it, stefano.menichetti@unifi.it.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Prof. Alessandro Degl'Innocenti.

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