DOI: 10.1002/ejoc.201001049

Synthesis of *S*-Acetyl Oligo-*p*-aryleneethynylene Tetrathiols

Omar Hassan Omar,[a] Francesco Babudri,*[b] Gianluca M. Farinola,[b] Francesco Naso,[b] and Alessandra Operamolla[b]

Dedicated to Professor Saverio Florio on the occasion of his 70th birthday

Keywords: Alkynes / C-C coupling / Heterocycles / Palladium / Sulfur

A novel class of tetrathiolated aryleneethynylene oligomers was obtained by the Cassar–Heck–Sonogashira coupling between *S*,*S*′-(5-ethynyl-1,3-phenylene)bis(methylene)diethanethioate (**1**) and aryl diiodides or dibromides. Although standard coupling conditions are effective in the case of iodo derivatives, the addition of free triphenylphosphane to the reaction mixture was required to overcome the slower reaction rate of dibromoarenes. Oligomers with an extended conjugated system could be obtained starting from a higher homologue of **1** by applying the same synthetic approach. These oligomers represent interesting molecular wires, potentially able to self-assemble on various substrates, including gold and other noble metals in the form of thin films or nanoparticles. The chelating arrangement of the thiol functionalities should ensure stable anchoring and would also represent an interesting novel feature in the study of single molecule conduction with respect to traditional monodentate systems.

Introduction

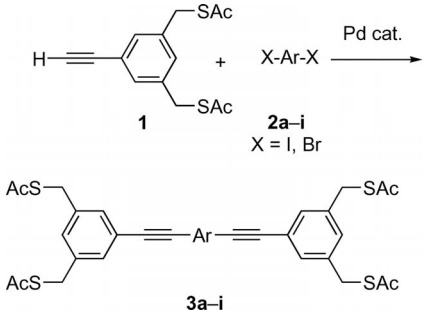
π-Conjugated oligomers with a well-defined structure are considered useful molecular materials for electronics and photonics[1] embracing the fabrication of devices such as OLEDs,[2] OTFTs,[3] and photovoltaic cells.[4] Moreover, they are model compounds in the study of the electronic properties of their corresponding polymers. In particular, oligo-*p*-aryleneethynylenes (OAEs)[5] have attracted special interest for their applications, including molecular electronics.[6] Indeed, many studies on OAEs have focused on the comprehension of electron transport through single molecules and on the interactions between molecules and electrodes.[7] These rigid rod-like structures exhibit some peculiar characteristics connected with the presence of C–C triple bonds: the conductivity may arise through extended π–orbital overlap, which is maximized when the molecule is planar.[8] As a consequence, the interest in OAEs as "molecular nanowires" is rapidly increasing.[6a,7,9] Molecular wires are usually equipped with a functional group on at least one terminus that is able to act as a chemical linker to a metal substrate. In this respect, thiol functionalities[10] have been widely employed as "alligator clips" to anchor conjugated oligomers on gold and other substrates.[11] Such conjugated thiols can find application in the preparation of self-assembled monolayers (SAMs) as modifiers of electrodes work-function,[12] or may be used to interface between proximal metallic probes for molecular electronics studies.[7,13] Furthermore, these metal–molecule assemblies can display some interesting features such as negative differential resistance[14] or switching behavior[15] that would enable applications of organic semiconductors in computing elements. In order to confer stability and reproducibility to these composite molecular architectures, the formation of a strong chemical bond between the oligomer and the metal is highly desirable. Up to now, different linking geometries have been considered,[7b,16] and methyl thioacetate functionalization was proven to be able to confer interesting features both to SAMs[17] and to metal–molecule–metal junctions.[18]

While major attention has been dedicated to the study of monodentate thiol systems, only little consideration has been given to chelating thiol-based monolayers[16] or molecular wires,[19] although the entropy-driven "chelate effect" would be in principle expected to enhance the stability of the molecule–metal bond. Therefore, appropriately designed chelating thiols could be employed to ensure a steady molecule–metal bond. In this respect, we have recently introduced a novel synthetic approach to *S*-acetyl oligoarylenedithiols[20] that are superior homologues of xylene-α,α′-dithiols.[16a] In recent times, these ligands have attracted renewed attention,[21] and in a parallel work[22] we demon-

[a] CNR-ICCOM Istituto di Chimica dei Composti OrganoMetallici,
Via Orabona 4, 70126 Bari, Italy
[b] Dipartimento di Chimica,
Università degli Studi Aldo Moro di Bari,
Via Orabona 4, 70126 Bari, Italy
Fax: +39-0805442129
E-mail: babudri@chimica.uniba.it
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001049.

strated their ability to bind to crystalline (111) gold through both sulfur atoms. Beside the advantages listed above, the chelating dithiol binding geometry would permit arrangement of the conjugated skeleton perpendicularly to the metal surface,[22] thus allowing a series of interesting studies in the field of molecular conductivity or in the engineering of composite molecular architectures.

In the framework of our extensive work devoted to the study of organometallic methodologies leading to the synthesis of conjugated organic materials,[23] and considering the interesting perspectives of OAE oligomers as molecular semiconductors, in this paper we report our results on the synthesis of a new class of tetrafunctional oligomers having a chelating dithiol geometry at both termini of the conjugated backbone. We selected the Cassar–Heck–Sonogashira[24] reaction, which represents by far the most general procedure for the preparation of OAEs, as the general synthetic approach to tetrathiolated systems (Scheme 1).

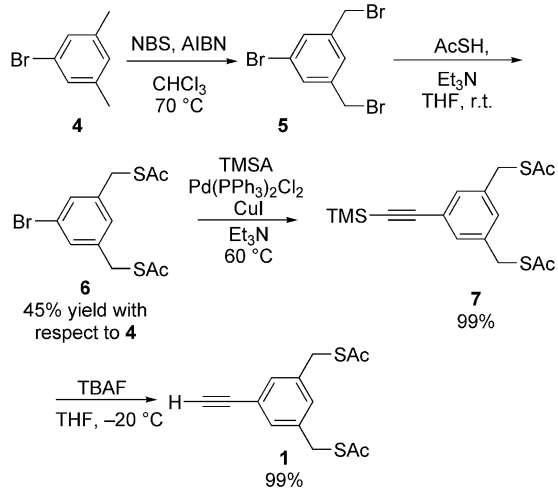


Scheme 1. General protocol for the preparation of OAE tetramethyl thiols.

In our view, ethynyl derivative **1** appears as a versatile intermediate for building OAEs with more complex architectures, and the Cassar–Heck–Sonogashira coupling of **1** with aromatic dihalides provides extension of the conjugation in one step. This synthetic strategy is convergent and allows the same arylethynyl intermediate to be used for the synthesis of a wide range of OAE structures. In particular, we have protected the thiol functionalities as acetic esters, considering the proven tolerability of the thiol ester groups to the Cassar–Heck–Sonogashira coupling reaction conditions[25] and the easy removal of the protecting groups.[26] In this paper we report the application of the synthetic strategy depicted in Scheme 1 to the synthesis of several OAEs having structure **3**, starting from different aryl dihalides. Moreover, by using a higher homologue of **1** we were able to obtain OAEs with a more extended π conjugated system.

Results and Discussion

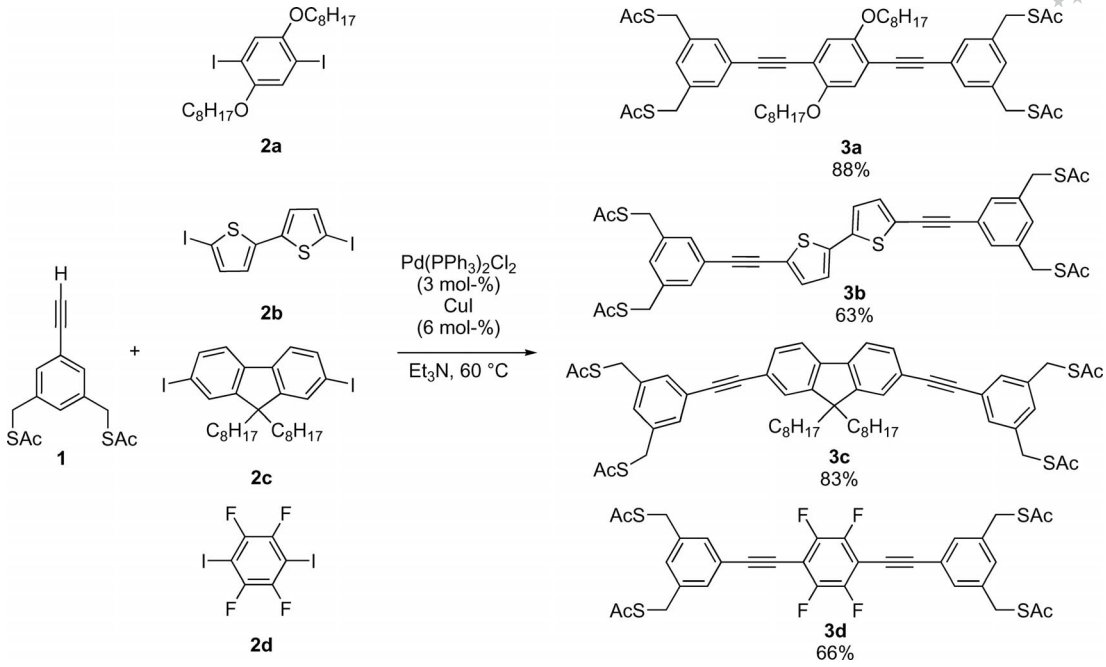
The synthesis of building block **1** consists of four simple steps, as reported in Scheme 2. Starting from commercially available 1-bromo-3,5-dimethylbenzene (**4**), bromination by employing a stoichiometric amount of NBS in the presence of AIBN was followed by reaction with thioacetic acid and triethylamine to afford bromide **6** in 45% yield with respect to **4**.[27] The subsequent step was Cassar–Heck–Sonogashira reaction of **6** with trimethylsilylacetylene (TMSA). In our case, the use of known conditions for the cross-coupling of derivatives bearing an *S*-acetyl group[25] {i.e., [$Pd(PPh_3)_2Cl_2$], CuI, and a solvent mixture of THF/diisopropylethylamine (1:1) under moderate heating} generated only the homocoupling product of trimethylsilylacetylene; bromide **6** was recovered unreacted. Halide **6** was also unreactive towards different alkynyl derivatives, for example, phenylacetylene, phenyltrimethylsilylacetylene, arylbis(ethynyl), and arylbis(trimethylsilylethynyl) derivatives, under various experimental conditions[28] and towards palladium complexes including catalysts with electron-rich phosphane ligands[28b,28c] that have been employed in synthetic protocols resulting among the most efficient reported so far. This behavior confirmed the strongly deactivating effect of the two thioacetylmethyl moieties in the relative 1,3-positions, as was also observed in our previous work on similar aryl bromides.[20] Such an effect should probably take place through competitive coordination of the two *S*-acetyl moieties to the catalyst.



Scheme 2. Synthesis of ethynyl derivative **1**.

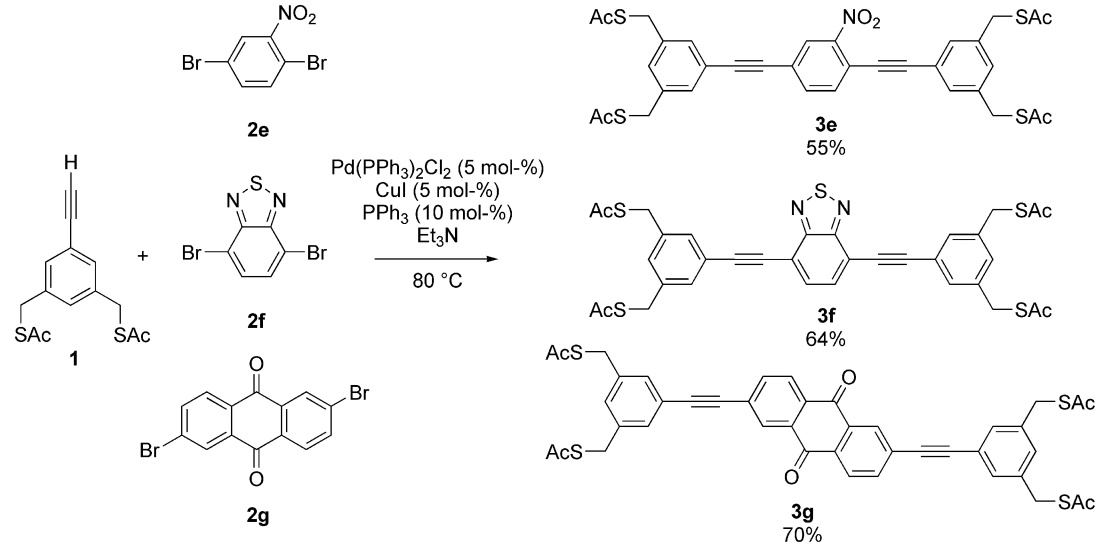
Although the use of THF as cosolvent was reported to improve the yields of the alkyne coupling reaction,[29] in our case the use of pure triethylamine as solvent[30] in the presence of $Pd(PPh_3)_2Cl_2$ (2 mol-%) and CuI (4 mol-%) at 60 °C was effective in obtaining intermediate **7** in high yield. The subsequent desilylation step, carried out by treating **7** with TBAF at –20 °C,[31] afforded desired ethynyl derivative **1** in quantitative yield as a white solid. Compound **1** reacted with a series of aryl diiodides and dibromides. As reported in Scheme 3, the coupling products of **1** with aryl diiodides were obtained in good to excellent yields. Electron-rich and electron-poor aryl iodides showed very good reactivity towards **1** under the same conditions adopted for the coupling of **6** with TMSA. Reactions were complete within 3 h and gave the corresponding products **3a**–**d** in the form of highly pure crystalline materials in good yields.

The higher reactivity of iodo derivatives in the Cassar–Heck–Sonogashira coupling is well established. However, aromatic or heteroaromatic iodides are often rather expens-

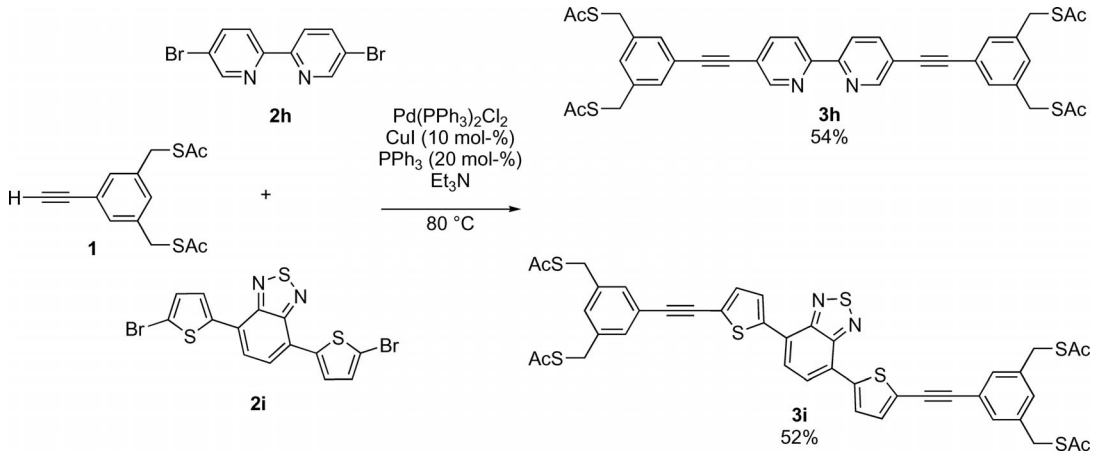


Scheme 3. Reaction of **1** with aryl diiodides.

ive and of limited availability. The corresponding dibromo derivatives are cheaper and more readily accessible, but, unfortunately, their reactivity is rather low with respect to their iodine counterparts. Also, in our case, dibromides gave unsatisfactory yields even with prolonged reaction times (24 to 48 h). For example, reaction of **1** with 2,5-dibromonitrobenzene (**2e**) gave desired oligomer **3e** (Scheme 4) in only 26% yield. However, we where able to perform the coupling reaction of less-reactive dibromides **2e**–**g** by employing an additional amount of triphenylphosphane in the reaction mixture. Under these conditions, the catalytic complex is considered to be longer lived, as the presence of more ligand prevents its dissociation.[29] As reported in Scheme 4, derivative **1** and aryl dibromides were treated in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol-%), CuI (5 mol-%), and an additional amount of PPh_3 (10 mol-%). These reaction conditions led to the formation of the expected oligomers in good yields. Double the amount of PPh_3 and CuI was adopted for the coupling reaction of dibromo heteroarylenes **2h** and **2i** with **1** (Scheme 5). Indeed, reaction of **1** in the presence of CuI (5 mol-%), the palladium catalyst, and triphenylphosphane (10 mol-%) afforded oligomer **3h** in only 7% overall yield. The lower reactivity of **2h** can also be ascribed to the coordinating ability of the bipyridine unit, which may interfere with the catalyst activity. However, **3h** was obtained in 54% yield after a reaction time of 24 h by increasing the amounts of CuI (10 mol-%) and triphenylphosphane (20 mol-%; see the Experimental Section). Comparable results were obtained in the case of **3i**. Compound **3h**, containing a bipyridine unit, was previously



Scheme 4. Reaction of **1** with aryl dibromides.

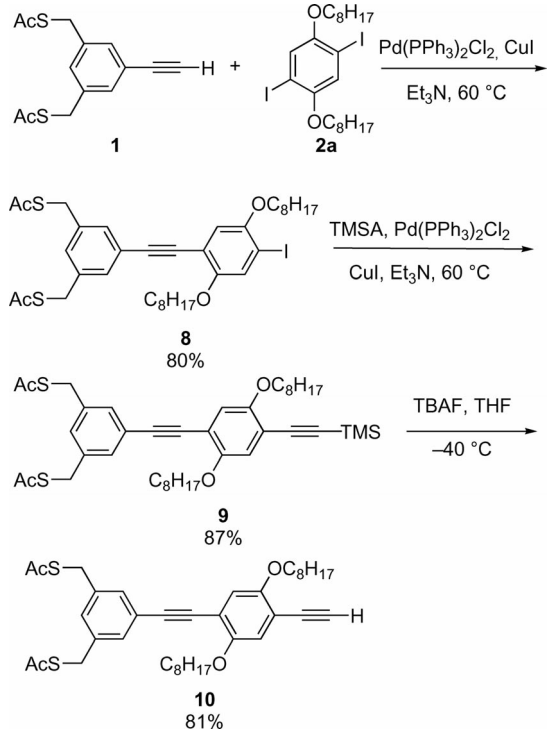


Scheme 5. Reaction of **1** with aryl dibromides with **2h** and **2i**.

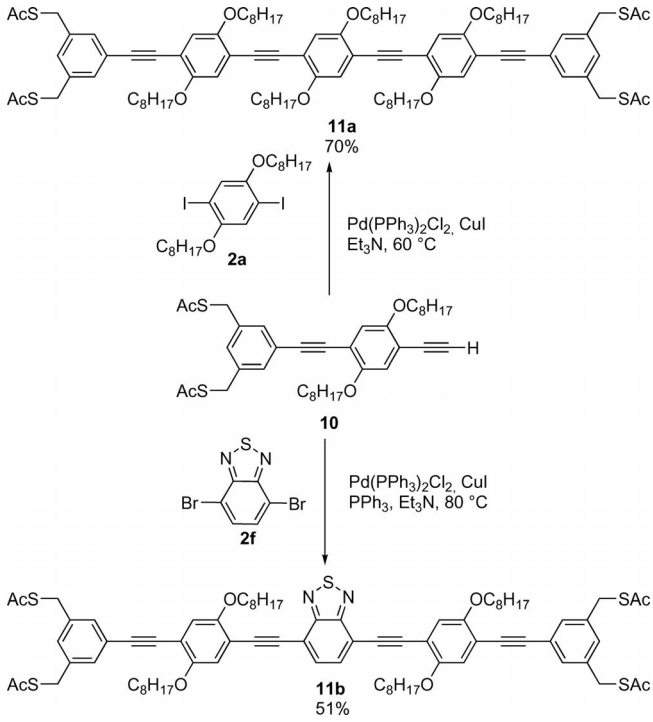
synthesized by Belaissaoui and co-workers.[32] In this case, a different synthetic sequence presenting a lower yield (30%) and employing more reactive aryl iodides was used. It is worth noting that in compounds **3a**–**i** the four thioacetyl groups were able to confer solubility in common organic solvents, allowing their easy purification by chromatography or crystallization. OAE oligomers **3a**–**i** are characterized by several features that make them promising materials for study of molecular electronics. Their rigid framework reduces the conformational flexibility, and in OAEs **3c**, **3f**, **3g**, and **3i**, a planar arrangement of the conjugated system is conferred by the presence of condensed aromatic rings. The double thiol functionalization at both terminal aromatic rings of all the oligomers appears also of interest for their use as linkers for the assembly of nanoparticles in 3D supramolecular structures.

Generally, OAEs containing cores capable of being oxidized or reduced are interesting candidates as "computing molecules".[15] In this respect, compounds **3e** and **3g** might be suitable for this purpose. Furthermore, compound **3i** is the first molecular wire containing a 4,7-dithienylbenzothiadiazole core, a widely employed acceptor unit that usually confers special optical properties to the resulting material,[33] and this may have a particular interest in organic photovoltaics applications. It is noteworthy that an entire family of thiolated OAEs was obtained by the same synthetic route, whereas, generally, the low reactivity of some halides, in particular bromides, requires the employment of different synthetic routes to afford the desired products in reasonable yields.[13a]

As a further extension of our synthetic procedure, we decided to test the feasibility of an iterative approach for the homologation of the conjugated system of **1** with the aim of obtaining longer molecular wires. This approach has been designed on the basis of the repetition of the iterative sequence in the presence of the *S*-acetyl groups, as depicted in Scheme 6. Therefore, we synthesized arylethynyl derivative **10**, the higher homologue of **1**, which can be obtained from **1** by a synthetic sequence based on the Cassar–Heck–Sonogashira reaction of aryl iodides. Compound **1** was treated with **2a** (3 equiv) to afford aryl iodide **8** in 80% yield. Subsequently, the reaction of **8** with TMSA gave trimethylsilyl aryne **9** in 87% yield. Building block **10** was obtained in 81% yield by reaction of **9** with TBAF at –40 °C in THF. As in the case of **1**, terminal aryne **10** could efficiently be coupled with dihalides under the same reaction conditions as those employed for **1**. Reaction of **10** with 2,5-bis(octyloxy)-1,4-diiodobenzene afforded OAE **11a** in good yield (70%) after a reaction time of 1 h. Compound **10** gave also satisfactory results when it was treated with 4,7-dibromobenzothiadiazole (**2f**), leading to the formation of product **11b** after 2 h as an orange material in 51% yield (Scheme 7).

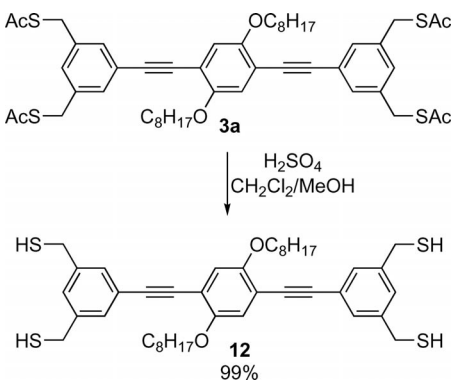


Scheme 6. Iterative synthetic approach to longer ethynyl derivatives.



Scheme 7. Reaction of **10** with dihalides **2a** and **2f**.

Finally, we were able to devise a straightforward protocol for the deprotection of the thioacetate functionality of these oligomers. Indeed, although it is not necessary to perform the deprotection prior to self-assembling these materials on gold,[34] there are a number of materials such as inorganic semiconductors, nanocrystals, silver, and other metals on which free thiol groups have a greater possibility to attach. A screening of deprotection conditions revealed that the formation of free thiol derivatives from the thiol esters that we synthesized can be easily achieved by employing sulfuric acid under mild conditions with the use of dichloromethane/methanol as the solvent. Deprotection of oligomer **3a**, reported in Scheme 8, was achieved under these conditions, and tetrathiol **12** could be isolated in quantitative yield as a highly pure yellow solid by crystallization from dichloromethane/methanol.



Scheme 8. Acid deprotection of **3a**.

Conclusions

In conclusion, by taking advantage of a synthetic tool based upon the Cassar–Heck–Sonogashira reaction between different halides and ethynyl building block **1**, we performed the synthesis of a novel class of OAEs bearing four acetylthiomethyl functionalities that are bonded on the terminal aryl rings in the relative 1,3-positions. The use of triethylamine as solvent and the addition of free triphenylphosphane to the reaction mixture represented essential variations of the coupling reaction conditions. The reaction also proceeded very well with aromatic and heteroaromatic bromides, which are coupling partners that are often more readily available and less expensive than their more reactive iodo counterparts. The oligomers obtained differ in the nature and the properties of the central aromatic core. The thiol functionalization confers chelating properties to the target compounds, which in principle would give origin to more stable assemblies of these molecules on inorganic conducting or semiconducting materials with respect to their monodentate counterparts, as established in the case of oligophenylenes with two *S*-acetyl methylthio groups in the 1,3-relative positions in our previous work.[22] Furthermore, the selected binding geometry should ensure steadiness to the derived metal–molecule–metal junction, thus generating an undoubtedly interesting system for single molecule conductivity studies or other applications. The compounds obtained herein or other materials that can be synthesized with the procedures set up in the present work can be considered promising architectures in the molecular electronic field.

Experimental Section

General: All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with dry solvents. All solvents were distilled immediately prior to use with the exception of triethylamine, which was distilled from KOH and then stored over molecular sieves under a nitrogen atmosphere. Tetrahydrofuran was distilled from benzophenone ketyl. Methanol was distilled from molecular sieves. Chloroform and dichloromethane were distilled from phosphorus pentoxide. Diiodides **2a**,[35] **2b**,[36] and **2c**[37] and dibromides **2g**,[38] **2h**,[39] and **2i**[40] were synthesized according to literature procedures. The syntheses of compounds **1** and **5**–**10** are reported in the Supporting Information. Other reagents were purchased at the highest commercial quality and used without further purification, with the exception of *N*-bromosuccinimide, which was crystallized from water. Silica gel 60 F254 aluminum sheets were used for analytical TLC analysis. Preparative column chromatography was carried out by using silica gel 60, 40–63 μm. Petroleum ether (PE) was the 40–60 °C boiling range fraction. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and IR spectroscopy, elemental analysis, and GC–MS analysis. GC analyses were performed with a gas chromatograph equipped with a SE-30 (methyl silicone, 30 m × 0.25 mm i.d.) capillary column and a FID detector. GC–MS analyses were performed with a gas chromatograph equipped with a SE-30 (methyl silicone, 30 m × 0.25 mm id) capillary column and an ion trap selective mass detector. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 400, 100,

and 376 MHz, respectively, or at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR), by using the residual proton peak of $CDCl_3$ at δ = 7.26 ppm or the signal of tetramethylsilane at δ = 0 ppm as internal standard for ^{1}H spectra, the signals of $CDCl_3$ at δ = 77 ppm or the signal of tetramethylsilane at δ = 0 ppm as internal standard for ^{13}C spectra and the ^{19}F signal of trichlorofluoromethane as internal standard at δ = 0 ppm for ^{19}F spectra. Melting points were obtained with a capillary melting point apparatus.

General Procedure for the Cassar–Heck–Sonogashira Cross-Coupling of Compound 1 with Aryl Diiodides: An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with $Pd(PPh_3)_2Cl_2$ (11 mg, 0.015 mmol, 3 mol-%), CuI (6 mg, 0.03 mmol, 6 mol-%), *S*,*S*′-(5-ethynyl-1,3-phenylene)bis(methylene)diethanethioate (**1**; 306 mg, 1.1 mmol), and the aryl iodide (0.5 mmol). Freshly distilled triethylamine (7 mL) was added, and the mixture was stirred for a few minutes at room temperature and then heated at 60 °C until almost complete disappearance of the aryl halide was observed. The reaction was monitored by TLC analysis. The reaction mixture was cooled to room temperature, neutralized with an aqueous solution of 5% HCl (30 mL), and extracted with dichloromethane (3 × 30 mL). The organic layers were collected, washed with a saturated solution of NaCl (3 × 30 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel.

***S*,*S*′,*S*″,*S*‴-{5,5′-[2,5-Bis(octyloxy)-1,4-phenylene]bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)}tetrakis(methylene)tetraethanethioate (3a):** The crude product was purified by silica gel chromatography (dichloromethane/PE, 80:20). Starting from diiodide **2a** (0.293 g), a yellow solid (0.391 g, 88% yield) was isolated. $C_{50}H_{62}O_6S_4$ (887.29): calcd. C 67.68, H 7.04, S 14.46; found C 67.70, H 7.18, S 14.65. M.p. 94–95 °C (dichloromethane/hexane) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (br. s, 4 H, 4 aromatic CH of the external rings), 7.17 (br. s, 2 H, 2 aromatic CH of the external rings), 6.99 (s, 2 H, 2 aromatic CH of the central ring), 4.08 (s, 8 H, 4 benzyl CH_2), 4.03 (t, J = 6.5 Hz, 4 H, 2 OCH_2CH$_2$), 2.37 (s, 12 H, 4 S-acetyl CH_3), 1.85 (quint., J = 6.5 Hz, 4 H, 2 O CH$_2$$CH_2CH_2$), 1.54 (quint., J = 6.5 Hz, 4 H, 2 CH_2), 1.22–1.43 (m, 16 H, 8 CH_2), 0.86 (t, J = 6.8 Hz, 6 H, 2 CH_3 of the alkoxy chain) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5 (C=O), 153.5, 138.2, 130.7, 129.1, 124.1, 117.0, 113.8, 94.1 (C≡C), 86.4 (C≡C), 69.7, 33.0, 32.0, 30.4, 29.43, 29.39, 29.36, 26.1, 22.7, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2864, 2213 (w, $\nu_{C\equiv C}$), 1693 (s, $\nu_{C=O}$), 1592, 1504, 1415, 1223, 1127, 623 cm^{-1}.

***S*,*S*′,*S*″,*S*‴-{5,5′-[2,2′-Bithiophene-5,5′-diylbis(ethyne-2,1-diyl)]-bis(benzene-5,3,1-triyl)}tetrakis(methylene)tetraethanethioate (3b):** The crude product was purified by silica gel chromatography (PE/dichloromethane/diethyl ether, 45:50:5). Starting from diiodide **2b** (0.209 g), a yellow solid (0.227 g, 63% yield) was isolated. M.p. 154–156 °C (dichloromethane/methanol). $C_{36}H_{30}O_4S_6$ (719.02): calcd. C 60.14, H 4.21, S 26.76; found C 59.77, H 4.51, S 26.42. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (br. s, 4 H, external rings), 7.16–7.19 (m, 4 H, 2 H of thiophene rings, 2 H of external rings), 7.08 (d, J = 3.8 Hz, 2 H, thiophene rings), 4.08 (s, 8 H, 4 benzyl CH_2), 2.37 (s, 12 H, 4 *S*-acetyl CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5 (C=O), 138.4, 138.1, 132.9, 130.4, 129.4, 124.0, 123.3, 122.2, 93.9 (C≡C), 82.9 (C≡C), 32.9, 30.4 ppm. IR (KBr): $\tilde{\nu}$ = 2917, 2200 (w, $\nu_{C\equiv C}$), 1690 (s, $\nu_{C=O}$), 1590, 1406, 1351, 1128, 957, 623 cm^{-1}.

***S*,*S*′,*S*″,*S*‴-{5,5′-[9,9-Dioctyl-9*H*-Fluorene-2,7-diylbis(ethyne-2,1-diyl)]bis(benzene-5,3,1-triyl)}tetrakis(methylene)tetraethanethioate (3c):** The crude product was purified by silica gel chromatography (PE/dichloromethane, 20:80). Starting from diiodide **2c** (0.321 g), a yellow oil (0.391 g, 83% yield) was isolated. $C_{57}H_{66}O_4S_4$ (943.40): calcd. C 72.57, H 7.05, S 13.60; found C 72.59, H 7.17, S 13.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.69 (d-like, $J \approx$ 8 Hz, 2 H, fluorene ring CH), 7.48–7.53 (m, 4 H, fluorene ring CH), 7.39 (br. s, 4 H, external rings CH), 7.17 (br. s, 2 H, external rings CH), 4.09 (s, 8 H, 4 benzyl CH_2), 2.37 (s, 12 H, 4 *S*-acetyl CH_3), 1.98 (m, 4 H, CH_2), 1.01–1.29 (m, 24 H, CH_2), 0.80 (t, J = 7.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8 (C=O), 151.1, 140.8, 138.4, 130.8, 129.1, 126.0, 124.0, 121.7, 120.0, 90.9 (C≡C), 89.1 (C≡C), 55.2, 40.3, 32.9, 31.8, 30.3, 30.0, 29.7, 29.2, 23.7, 22.6, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 2209 (w, $\nu_{C\equiv C}$), 1694 (s, $\nu_{C=O}$), 1594, 1470, 1353, 1224, 953, 630 cm^{-1}.

***S*,*S*′,*S*″,*S*‴-[5,5′-(Perfluoro-1,4-phenylene)bis(ethyne-2,1-diyl)bis-(benzene-5,3,1-triyl)]tetrakis(methylene)tetraethanethioate (3d):** The crude product was purified by silica gel chromatography (dichloromethane/PE/diethyl ether, 50:45:5). Starting from diiodide **2d** (0.201 g), a white solid (0.232 g, 66% yield) was isolated. M.p. 163–164 °C (dichloromethane/methanol). $C_{34}H_{26}F_4O_4S_4$ (702.83): calcd. C 58.10, H 3.73, S 18.25; found C 57.87, H 3.67, S 18.11. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (br. s, 4 H, external rings CH), 7.27 (br. s, 2 H, external rings CH), 4.09 (s, 8 H, 4 benzyl CH_2), 2.38 (s, 12 H, 4 *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7 (C=O), 146.5 (dm, $J_{H,F}$ = 249.7 Hz, *C*-F), 138.7, 131.0, 130.7, 122.2, 104.7 (m, CF-*C*-C≡C), 102.3 (C≡C), 74.9 (C≡C), 32.7, 30.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –137.3 (s, 4 F) ppm. IR (KBr): $\tilde{\nu}$ = 2228 (w, $\nu_{C\equiv C}$), 1686 (s, $\nu_{C=O}$), 1492, 1132, 982, 628 cm^{-1}.

General Procedure for the Cassar–Heck–Sonogashira Cross-Coupling of Compound 1 with Aryl Bromides: An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with triphenylphosphane (13 mg, 0.05 mmol, 10 mol-%), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol, 5 mol-%), CuI (5 mg, 0.025 mmol, 5 mol-%), *S*,*S*′-(5-ethynyl-1,3-phenylene)bis (methylene)diethanethioate (**1**; 306 mg, 1.1 mmol), aryl bromide (0.5 mmol), and finally, with freshly distilled triethylamine (7 mL). The mixture was stirred for a few minutes at room temperature and then heated at 80 °C until almost complete disappearance of the aryl halide was observed. The completion of the reaction was monitored by TLC analysis. The reaction mixture was cooled to room temperature, neutralized with an aqueous solution of 5% HCl (50 mL), and extracted with dichloromethane (3 × 50 mL). The organic layers were collected, washed with a saturated solution of NaCl, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel.

***S*,*S*′,*S*″,*S*‴-[5,5′-(2-Nitro-1,4-phenylene)bis(ethyne-2,1-diyl)bis-(benzene-5,3,1-triyl)]tetrakis(methylene)tetraethanethioate (3e):** The crude product was purified by silica gel chromatography (dichloromethane/PE/diethyl ether, 70:27:3). Starting from dibromide **2e** (0.140 g), a reddish solid (0.185 g, 55% yield) was isolated. M.p. 99–100 °C (dichloromethane/methanol). $C_{34}H_{29}NO_6S_4$ (675.86): calcd. C 60.42, H 4.32, N 2.07, S 18.98; found C 60.11, H 4.71, N 1.94, S 18.92. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.23 (m, 1 H, internal ring CH), 7.71–7.65 (m, 2 H, internal ring CH), 7.39 (br. s, 2 H, external ring CH), 7.37 (br. s, 2 H, external ring CH) 7.24 (br. s, 1 H, external rings CH), 7.22 (br. s, 1 H, external rings CH), 4.08 (s, 8 H, benzyl CH_2), 2.38 (s, 12 H, *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5 (C=O), 149.3, 138.6, 138.5, 135.1, 134.4, 131.0, 130.8, 130.3, 130.0, 127.5, 123.9, 122.8, 122.6, 117.8, 98.2 (C≡C), 92.9 (C≡C), 87.1 (C≡C), 85.1 (C≡C),

32.8, 30.4 ppm. IR (KBr): $\tilde{\nu}$ = 2916, 2196 (w, $\nu_{C\equiv C}$), 1691 (s, $\nu_{C=O}$), 1542 (ν_{as,NO_2}), 1340 (ν_{s,NO_2}), 1130, 1097, 959, 624 cm^{-1}.

***S*,*S*′,*S*′′,*S*′′′-{5,5′-[Benzo[*c*](1,2,5)thiadiazole-4,7-diylbis(ethyne-2,1-diyl)]bis(benzene-5,3,1-triyl)}tetrakis(methylene)tetraethanethioate (3f):** The crude product was purified by silica gel chromatography (dichloromethane/ethyl acetate/PE, 89:1:10). Starting from dibromide **2f** (0.147 g), a yellow solid (0.221 g, 64% yield) was isolated. M.p. 123–124 °C (dichloromethane/methanol). $C_{34}H_{28}N_2O_4S_5$ (688.83): calcd. C 59.28, H 4.10, N 4.07, S 23.27; found C 59.15, H 4.28, N 3.81, S 23.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 2 H, benzothiadiazole ring CH), 7.48 (br. s, 4 H, external rings CH), 7.24 (br. s, 2 H, external rings CH), 4.11 (s, 8 H, 4 benzyl CH_2), 2.38 (s, 12 H, 4 *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8 (C=O), 154.2, 138.5, 132.6, 131.1, 130.1, 123.1, 117.0, 96.8 (C≡C), 85.6 (C≡C), 32.8, 30.3 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2207 (w, $\nu_{C\equiv C}$), 1695 (s, $\nu_{C=O}$), 1594, 1404, 1352, 1127, 958, 623 cm^{-1}.

***S*,*S*′,*S*′′,*S*′′′-[5,5′-(9,10-Dioxo-8a,9,10,10a-tetrahydroanthracene-2,6-diyl)bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)]tetrakis(methylene)tetraethanethioate (3g):** The crude product was purified by silica gel chromatography (PE/dichloromethane/diethyl ether, 17:80:3). Starting from dibromide **2g** (0.183 g), a yellow solid (0.267 g, 70% yield) was isolated. M.p. 211–213 °C (dichloromethane/methanol). $C_{42}H_{32}O_6S_4$ (760.96): calcd. C 66.29, H 4.24, S 16.86; found C 66.09, H 4.23, S 16.70. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.39 (br. s, 2 H, anthraquinone ring CH), 8.29 (d-like, $J \approx 8$ Hz, 2 H, anthraquinone ring CH), 7.87 (d-like, $J \approx 8$ Hz, 2 H, anthraquinone ring CH), 7.39 (br. s, 4 H, external rings CH), 7.23 (br. s, 2 H, external rings CH), 4.10 (s, 8 H, 4 benzyl CH_2), 2.39 (s, 12 H, 4 *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (acetyl groups, C=O), 181.7 (anthraquinone unit, C=O), 138.6; 136.4, 133.3, 132.1, 130.9, 130.2, 130.0, 129.4, 127.4, 122.8, 93.7 (C≡C), 88.3 (C≡C), 32.8, 30.4 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2204 (w, $\nu_{C\equiv C}$), 1691 (s, $\nu_{C=O}$), 1670 (s, $\nu_{C=O}$), 1595, 1306, 1289, 1130, 955, 625 cm^{-1}.

Procedure for the Cassar–Heck–Sonogashira Cross-Coupling of Compound 1 with Compounds 2h and 2i: An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with triphenylphosphane (26 mg, 0.10 mmol, 20 mol-%), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol, 5 mol-%), CuI (10 mg, 0.05 mmol, 10 mol-%), *S*,*S*′-(5-ethynyl-1,3-phenylene)bis(methylene)diethanethioate (**1**; 306 mg, 1.1 mmol), the aryl bromide (0.5 mmol), and finally, freshly distilled triethylamine (7 mL). The mixture was stirred for a few minutes at room temperature and then heated at 80 °C for 24 h. The reaction completion was monitored by TLC analysis. The reaction mixture was cooled to room temperature, neutralized with an aqueous solution of 5% HCl (30 mL), and extracted with dichloromethane (3 × 30 mL). The organic layers were collected, washed with a saturated solution of NaCl (3 × 30 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel.

***S*,*S*′,*S*′′,*S*′′′-{5,5′-[2,2′-Bipyridine-5,5′-diylbis(ethyne-2,1-diyl)]bis(benzene-5,3,1-triyl)}tetrakis(methylene)tetraethanethioate (3h):** The crude product was purified by silica gel chromatography (chloroform/PE/diethyl ether, 55:30:15). Starting from dibromide **2h** (0.157 g), a white solid (0.181 g, 54% yield) was isolated. M.p. 174–176 °C (dichloromethane/methanol). $C_{38}H_{32}N_2O_4S_4$ (708.94): calcd. C 64.38, H 4.55, N 3.95, S 18.09; found C 64.23, H 4.18, N 3.82, S 18.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (br. s, 2 H, bipyridine CH), 8.43 (d, J = 8.0 Hz, 2 H, bipyridine CH), 7.94 (d-like, $J \approx 8.0$ Hz, 2 H, bipyridine CH), 7.39 (br. s, 4 H, external rings CH), 7.21 (br. s, 2 H, external rings CH), 4.10 (s, 8 H, benzyl CH_2), 2.39 (s, 12 H, *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7 (C=O), 154.0, 151.6, 139.3, 138.5, 130.8, 129.7, 123.1, 120.6, 120.2, 93.1 (C≡C), 86.7 (C≡C), 32.9, 30.4 ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2916, 2204 (w, $\nu_{C\equiv C}$), 1685 (s, $\nu_{C=O}$), 1594, 1466, 1354, 1134, 1102, 953, 632 cm^{-1}.

***S*,*S*′,*S*′′,*S*′′′-[5,5′-{5,5′-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(thiophene-5,2-diyl)}bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)]-tetrakis(methylene)tetraethanethioate (3i):** The crude product was purified by silica gel chromatography (dichloromethane/ PE/diethyl ether, 70:28:2). Starting from dibromide **2i** (0.229 g), a red solid (0.224 g, 52% yield) was isolated. M.p. 139–141 °C (dichloromethane/methanol). $C_{42}H_{32}N_2O_4S_7$ (853.18): calcd. C 59.13, H 3.78, N 3.28, S 26.31; found C 59.33, H 3.72, N 3.33, S 26.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 3.9 Hz, 2 H, thiophene rings CH), 7.89 (s, 2 H, benzothiadiazole ring), 7.37 (br. s, 4 H, external rings CH), 7.33 (d, J = 3.9 Hz, 2 H thiophene rings CH), 7.18 (br. s, 2 H, external rings CH), 4.09 (s, 8 H, benzyl CH_2), 2.38 (s, 12 H, *S*-acetyl CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (C=O), 152.2, 140.5, 138.4, 132.9, 131.5, 130.4, 129.4, 127.4, 125.5, 124.5, 123.4, 94.5 (C≡C), 83.4 (C≡C), 32.9, 30.4 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2190 (w, $\nu_{C\equiv C}$), 1695 (s, $\nu_{C=O}$), 1590, 1406, 1350, 1130, 1096, 953, 622 cm^{-1}.

***S*,*S*′,*S*′′,*S*′′′-[5,5′-{4,4′-[2,5-Bis(octyloxy)-1,4-phenylene]bis(ethyne-2,1-diyl)bis[2,5-bis(octyloxy)-4,1-phenylene]}bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)]tetrakis(methylene)tetraethanethioate (11a):** An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with $Pd(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol, 3 mol-%), CuI (3 mg, 0.014 mmol, 6 mol-%), **10** (317 mg, 0.5 mmol), 1,4-diiodo-2,5-bis(octyloxy)benzene (135 mg, 0.23 mmol), and freshly distilled triethylamine (5 mL). The mixture was stirred for a few minutes at room temperature and then heated at 60 °C until almost complete disappearance of the aryl halide was observed. The reaction was monitored by TLC analysis, and after 1 h, the mixture was cooled to room temperature, neutralized with an aqueous solution of 5% HCl (15 mL), and extracted with dichloromethane (3 × 25 mL). The organic layers were collected, washed with a saturated solution of NaCl, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel (dichloromethane/PE, 9:1).A yellow-greenish solid (258 mg, 70% yield) was isolated. M.p. 98–100 °C (dichloromethane/methanol). $C_{98}H_{134}O_{10}S_4$ (1600.37): calcd. C 73.55, H 8.44, S 8.01; found C 73.17, H 8.09, S 8.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (br. s, 4 H, dithiolated ring CH), 7.16 (br. s, 2 H, dithiolated ring CH), 6.99–7.06 (m, 6 H, dialkoxy substituted rings CH), 4.08 (s, 8 H, benzyl CH_2), 4.08–4.06 (m, 12 H, OCH_2CH_2), 2.37 (s, 12 H, *S*-acetyl CH_3), 1.80–1.91 (m, 12 H, alkyl chain CH_2), 1.46–1.56 (m, 12 H, alkyl chain CH_2), 1.20–1.43 (m, 48 H, alkyl chain CH_2), 0.81–0.91 (m, 18 H, $-CH_2CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6 (C=O), 153.54, 153.40, 153.37, 138.2, 130.7, 129.1, 124.1, 117.3, 117.1, 114.4, 114.3, 113.7, 94.1 (C≡C), 91.6 (C≡C), 91.5 (C≡C), 86.5 (C≡C), 69.8, 69.7, 33.0, 31.9, 30.4, 29.47, 29.41, 26.17, 26.10, 26.06, 22.8, 14.2 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2851, 2198 (w, $\nu_{C\equiv C}$), 1695 (s, $\nu_{C=O}$), 1591, 1511, 1425, 1211, 1132, 1048, 954, 624 cm^{-1}.

***S*,*S*′,*S*′′,*S*′′′-{5,5′-(4,4′-{Benzo[*c*][1,2,5]thiadiazole-4,7-diylbis(ethyne-2,1-diyl)}bis[2,5-bis(octyloxy)-4,1-phenylene)]bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)}tetrakis(methylene) Tetraethanethioate (11b):** An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with $Pd(PPh_3)_2Cl_2$ (8 mg, 0.012 mmol, 5 mol-%), CuI

(2 mg, 0.012 mmol, 5 mol-%), triphenylphosphane (6 mg, 0.023 mmol, 10 mol-%), **10** (317 mg, 0.5 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (68 mg, 0.23 mmol), and freshly distilled triethylamine (10 mL). The mixture was stirred for a few minutes at room temperature and then heated at 80 °C until the reaction was complete (TLC analysis). After 2 h the reaction mixture was then cooled to room temperature, neutralized with an aqueous solution of 5% HCl (50 mL), and extracted with dichloromethane (3 × 50 mL). The organic layers were collected, washed with a saturated solution of NaCl, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel (dichloromethane/PE/diethyl ether, 58:40:2). An orange solid (165 mg, 51% yield) was isolated. M.p. 136–137 °C (dichloromethane/methanol). $C_{82}H_{100}N_2O_8S_5$ (1402.01): calcd. C 70.25, H 7.19, N 2.00, S 11.44; found C 69.93, H 7.25, N 1.89, S 12.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 2 H, benzothiadiazole ring CH), 7.36 (br. s, 4 H, dithiolated ring CH), 7.18 (br. s, 2 H, dithiolated ring CH), 7.14 (br. s, 2 H, dialkoxy substituted rings), 7.04 (br. s, 2 H, dialkoxy substituted rings CH), 4.03–4.12 (m, 16 H, benzyl CH_2 and O*C*H_2CH$_2$-), 2.37 (s, 12 H, *S*-acetyl CH_3), 1.82–1.97 (m, 8 H, alkyl chain CH_2), 1.50–1.65 (m, 8 H, alkyl chain CH_2), 1.22–1.46 (m, 32 H, alkyl chain CH_2), 0.81–0.92 (m, 12 H, -CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5 (C=O), 154.2, 154.0, 153.5, 138.2, 132.2, 130.7, 129.2, 124.0, 117.2, 117.0, 116.8, 114.7, 113.2, 94.6 (C≡C), 94.3 (C≡C), 90.9 (C≡C), 86.4 (C≡C), 69.75, 69.70, 32.98, 31.90, 30.38, 29.53, 29.44, 29.40, 26.14, 22.74, 14.18 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 2849, 2206 (w, $\nu_{C\equiv C}$), 1697 (s, $\nu_{C=O}$), 1594, 1508, 1416, 1220, 1130, 1033, 801, 629 cm^{-1}.

5,5′-[2,5-Bis(octyloxy)-1,4-phenylene]bis(ethyne-2,1-diyl)bis(benzene-5,3,1-triyl)tetramethanethiol (12): An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen (3×). Then it was charged with **3a** (200 mg, 0.23 mmol), dry dichloromethane (7 mL), and dry methanol (7 mL). The mixture was cooled using an ice bath, and concentrated H_2SO_4 (0.8 mL) was slowly added. The mixture was warmed to room temperature and stirred for a few minutes and then heated at 50 °C for 12 h. After this time, monitoring by TLC showed the complete disappearance of the substrate. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. Neutralization of the excess amount of acid with a saturated aqueous solution of $NaHCO_3$ was followed by extraction with dichloromethane (3 × 50 mL). The organic phase was collected, washed with saturated aqueous NaCl (3 × 100 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by crystallization (dichloromethane/methanol, 2×). A yellow solid (160 mg, 99% yield) was isolated. M.p. 225–227 °C (dichloromethane/hexane). $C_{42}H_{54}O_2S_4$ (719.14): calcd. C 70.15, H 7.57, S 17.84; found C 70.09, H 7.43, S 17.99. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (br. s, 4 H, external rings CH), 7.27 (br. s, 2 H, external ring CH), 7.01 (s, 2 H, internal ring CH), 4.04 (t, *J* = 6.4 Hz, 4 H, 2 O*C*H_2CH$_2$-), 3.72 (d, *J* = 7.7 Hz, 8 H, benzyl CH_2), 1.88 (quint., *J* = 6.8 Hz, 4 H, alkyl chain CH_2), 1.79 (t, *J* = 7.7 Hz, 4 H, -CH_2S*H*), 1.65–1.50 (m, 4 H, alkyl chain CH_2), 1.45–1.25 (m, 16 H, alkyl chain CH_2), 0.87 (t, *J* = 6.7 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 141.8, 129.8, 127.8, 124.1, 117.0, 113.9, 94.3 (C≡C), 86.3 (C≡C), 69.6, 31.9, 29.43, 29.37, 29.32, 28.57, 26.11, 22.69, 14.12 ppm. IR (KBr): $\tilde{\nu}$ = 2915, 2867, 2272 (w, ν_{S-H}), 2157 (w, $\nu_{C\equiv C}$), 1684 (s, $\nu_{C=O}$), 1594, 1506, 1409, 1220, 1031, 872, 696 cm^{-1}.

Supporting Information (see footnote on the first page of this article): Synthetic procedures and characterization data for compounds **1** and **5**–**10**.

Acknowledgments

This work was financially supported by Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), "Progetto PRIN 2007 PBWN44" and by Università degli Studi Aldo Moro di Bari.

[1] K. Müllen, G. Wegner (Eds.), *Electronic Materials: The Oligomer Approach*, Wiley-VCH, New York, **1998**.
[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539–541.
[3] G. Horowitz, *Adv. Mater.* **1998**, *10*, 365–377; H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* **2001**, *34*, 359–369.
[4] S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324–1338.
[5] H. Meier in *Carbon Rich Compounds* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, pp. 476–528.
[6] a) J. M. Tour in *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture, and Programming*, World Scientific Publishing, River Edge, NJ, **2003**; b) R. L. McCreery, A. J. Bergren, *Adv. Mater.* **2009**, *21*, 4303–4322; M. A. Ratner, *Mater. Today* **2002**, *5*, 20–27; C; c) Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541–548.
[7] a) L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **1996**, *271*, 1705–1707; M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252–254; C. Kergueris, J. P. Bourgoin, S. Palacin, *Nanotechnology* **1999**, *10*, 8–13; J. M. Seminario, C. E. De La Cruz, P. A. Derosa, *J. Am. Chem. Soc.* **2001**, *123*, 5616–5617; G. J. Ashwell, B. Urasinska, C. Wang, M. R. Bryce, I. Grace, C. J. Lambert, *Chem. Commun.* **2006**, 4706–4708; C. Risko, C. D. Zangmeister, Y. Yao, T. M. J. Marks, J. M. Tour, M. A. Ratner, R. D. Van Zee, *J. Phys. Chem. C* **2008**, *112*, 13215–13225; Q. Lu, K. Liu, H. Zhang, Z. Du, X. Wang, F. Wangm, *ACS Nano* **2009**, *3*, 3861–3868; H. P. Yoon, M. M. Maitani, O. M. Cabarcos, L. Cai, T. S. Mayer, D. L. Allara, *Nano Lett.* **2010**, *10*, 2897–2902; b) M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänish, D. Beckmann, M. Fischer, *Angew. Chem. Int. Ed.* **2003**, *42*, 5834–5838.
[8] D. R. Maulding, B. G. Roberts, *J. Org. Chem.* **1969**, *34*, 1734–1736; P. V. James, P. K. Sudeep, C. H. Suresh, K. G. Thomas, *J. Phys. Chem. A* **2006**, *110*, 4329–4337; P. K. Sudeep, P. V. James, K. G. Thomas, P. V. Kamat, *J. Phys. Chem. A* **2006**, *110*, 5642–5649.
[9] S. Martin, I. Grace, M. R. Bryce, C. Wang, R. Jitchati, A. S. Batsanov, S. J. Higgings, C. J. Lambert, R. J. Nichols, *J. Am. Chem. Soc.* **2010**, *132*, 9157–9164; K. Liu, G. Li, X. Wang, F. Wang, *J. Phys. Chem. C* **2008**, *112*, 4342–4349; R. Huber, M. T. Gonzalez, S. Wu, M. Langer, S. Grunder, V. Horhoiu, M. Mayor, M. R. Bryce, C. Wang, R. Jitchati, C. Schonenberger, M. Calame, *J. Am. Chem. Soc.* **2008**, *130*, 1080–1084; F. Maya, S. H. Chanteau, L. Cheng, M. P. Stewart, J. M. Tour, *Chem. Mater.* **2005**, *17*, 1331–1345.
[10] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1169.
[11] J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804.
[12] G. Heimel, L. Romaner, E. Zojer, J.-L. Bredas, *Acc. Chem. Res.* **2008**, *41*, 721–729.
[13] a) J. W. Ciszek, J. M. Tour, *Tetrahedron Lett.* **2004**, *45*, 2801–2803; b) A. K. Flatt, Y. Yao, F. Maya, J. M. Tour, *J. Org. Chem.* **2004**, *69*, 1752–1755; F. Maya, J. M. Tour, *Tetrahedron* **2004**, *60*, 81–92; Z. F. Shi, L. J. Wang, H. Wang, X. P. Cao, H. L. Zhang, *Org. Lett.* **2007**, *9*, 595–598.
[14] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550–1552; J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **2000**, *122*, 3015–3020; J. M. Seminario, A. G. Zacarias, P. A. Derosa, *J. Phys. Chem. A* **2001**, *105*, 791–795;

M. A. Reed, J. Chen, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **2001**, *78*, 3735–3738.

[15] V. Meded, A. Bagrets, A. Arnold, F. Evers, *Small* **2009**, *5*, 2218–2223; Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **2001**, *292*, 2303–2307; A. M. Moore, A. A. Dameron, B. A. Mantooth, R. K. Smith, D. J. Fuchs, J. W. Ciszek, F. Maya, Y. Yao, J. M. Tour, P. S. Weiss, *J. Am. Chem. Soc.* **2006**, *128*, 1959–1967; J. He, Q. Fu, S. Lindsay, J. W. Ciszek, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 14828–14835; E. H. Van Dijk, D. J. T. Myles, M. H. van der Veen, J. C. Hummelen, *Org. Lett.* **2006**, *8*, 2333–2336; J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, J. M. Tour, *Appl. Phys. Lett.* **2000**, *77*, 1224–1226.

[16] a) G. T. Lee, K. Kim, M. S. Kim, *J. Phys. Chem.* **1991**, *95*, 9950–9955; N. Garg, T. R. Lee, *Langmuir* **1998**, *14*, 3815–3819; K. V. G. K. Murty, M. Venkataramanan, T. Pradeep, *Langmuir* **1998**, *14*, 5446–5456; S. W. Joo, S. W. Han, K. Kim, *J. Phys. Chem. B* **1999**, *103*, 10831–10837; T. Pradeep, C. Evans, J. Shen, R. G. Cooks, *J. Phys. Chem. B* **1999**, *103*, 5304–6310; S. Rifai, M. Morin, *J. Electroanal. Chem.* **2003**, *277–289*, 550–551; N. Garg, E. Carrasquillo-Molina, T. R. Lee, *Langmuir* **2002**, *18*, 2717–2726; N. Garg, J. M. Friedman, T. R. Lee, *Langmuir* **2000**, *16*, 4266–4271; b) T. Kitagawa, Y. Idomoto, H. Matsubara, D. Hobara, T. Kakiuchi, T. Okazaki, K. Komatsu, *J. Org. Chem.* **2006**, *71*, 1362–1369; c) A. Fragoso, N. Laboria, D. Latta, C. K. O'Sullivan, *Anal. Chem.* **2008**, *80*, 2556–2563; C. W. Spangler, B. D. Spangler, E. S. Tarter, Z. Suo, *Polym. Prepr.* **2004**, *45*, 524–525; K. V. Gobi, H. Iwasaka, N. Miura, *Biosens. Bioelectron.* **2007**, *22*, 1382–1389; F. Nakamura, E. Ito, T. Hayashi, M. Hara, *Colloids Surf. A* **2006**, *495*, 284–285; A. Subramanian, J. Irudayaraj, T. Ryan, *Sens. Actuators B* **2006**, *114*, 192–198.

[17] Y. T. Tao, C. C. Wu, Y. Y. Eu, W. L. Lin, *Langmuir* **1997**, *13*, 4018–4023; M. Buck, M. Grunze, *J. Electroanal. Chem.* **2002**, *524–525*, 62–67; A. Shaporenko, M. Brunnbauer, A. Terfort, L. S. O. Johansson, M. Grunze, M. Zharnikov, *Langmuir* **2005**, *21*, 4370–4375; H. T. Rong, S. Frey, M. Yang, M. Zharnikov, M. Buck, M. Wühn, Ch. Wöll, G. Helmchen, *Langmuir* **2001**, *17*, 1582–1593; K. Heister, H.-T. Rong, M. Buck, M. Zharnikov, M. Grunze, L. S. O. Johansson, *J. Phys. Chem. B* **2001**, *105*, 6888–6894; P. Cyganik, H.-T. Felgenhauer, M. Rong, M. Buck, Z. Postawa, *Electron Technol.* **2000**, *33*, 337; A. Shaporenko, M. Brunnbauer, A. Terfort, M. Grunze, M. Zharnikov, *J. Phys. Chem. B* **2004**, *108*, 14462–14469; W. Azzam, A. Bashir, A. Terfort, T. Strunskus, Ch. Wöll, *Langmuir* **2006**, *22*, 3647–3655.

[18] T. T. Liang, Y. Naitoh, M. Ho-rikawa, T. Ishida, W. Mizutani, *J. Am. Chem. Soc.* **2006**, *128*, 13720–13726.

[19] Y. Xing, T.-H. Park, R. Venkatramani, S. Keinan, D. N. Beratan, M. J. Therien, E. Borguet, *J. Am. Chem. Soc.* **2010**, *132*, 7946–7956; T. P. Park, M. J. Therien, *Org. Lett.* **2007**, *9*, 2779–2782; R. Colorado Jr., R. J. Villazana, T. R. Lee, *Langmuir* **1998**, *14*, 6337–6340; A. V. Tivanski, Y. He, E. Borguet, H. Liu, G. C. Walker, D. H. Waldeck, *J. Phys. Chem. B* **2005**, *109*, 5398–5402; Z. Li, D. S. Kosov, *J. Phys. Chem. B* **2006**, *110*, 19116–19120.

[20] A. Operamolla, O. Hassan Omar, F. Babudri, G. M. Farinola, F. Naso, *J. Org. Chem.* **2007**, *72*, 10272–10275.

[21] J. K. Lim, Y. Kim, O. Kwon, S. W. Joo, *ChemPhysChem* **2008**, *9*, 1781–1787; J. K. Lim, O. Kwon, S. W. Joo, *J. Phys. Chem. C* **2008**, *112*, 6816–6821.

[22] G. Bruno, F. Babudri, A. Operamolla, G. V. Bianco, M. Losurdo, M. M. Giangregorio, O. Hassan Omar, F. Mavelli, G. M. Farinola, P. Capezzuto, F. Naso, *Langmuir* **2010**, *26*, 8430–8440.

[23] For reviews, see: F. Babudri, G. M. Farinola, F. Naso, R. Ragni, *Chem. Commun.* **2007**, 1003–1022; F. Babudri, G. M. Farinola, F. Naso, *J. Mater. Chem.* **2004**, *14*, 11–34; G. M. Farinola, F. Babudri, A. Cardone, O. Hassan Omar, F. Naso, *Pure Appl. Chem.* **2008**, *80*, 1735–1746.

[24] J. A. Mardsen, M. M. Haley in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH Weinheim, **2004**, vol. 2, pp. 317–394; L. Cassar, *J. Organomet. Chem.* **1975**, *93*, 253–257; F. R. Heck, *J. Organomet. Chem.* **1975**, *93*, 259–263; K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *50*, 4467–4469.

[25] R. P. Hsung, J. R. Babcock, C. E. D. Chidsey, L. R. Sita, *Tetrahedron Lett.* **1995**, *36*, 4525–4528.

[26] T. W. Greene, P. G. M. Wuts (Eds.), *Protective Groups in Organic Synthesis*, 3rd ed., John Wiley & Sons, Inc. New York, **1999**.

[27] Q. Li, C. A. V. Rukavishnikov, A. Phadke, M. D. Lee, D. H. La-Muyon, P. A. Pethukov, J. F. W. Keana, *Tetrahedron Lett.* **1999**, *40*, 6353–6356; Q. Li, C. Jin, P. A. Petukhov, A. V. Rukavishnikov, T. O. Zaikova, A. Phadke, D. H. La-Munyon, M. D. Lee, J. F. W. Keana, *J. Org. Chem.* **2004**, *69*, 1010–1019 for comparison of the radical bromination step.

[28] For a selection of the procedures that were investigated, see ref.[25] a) A. Mori, J. Kawashima, T. Shimada, M. Suguro, K. Hirabayashi, Y. Nishihara, *Org. Lett.* **2000**, *2*, 2935–2937; b) T. Hundertmark, A. F. Littke, S. L. Buchwald, G. C. Fu, *Org. Lett.* **2000**, *2*, 1729–1731; c) D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2003**, *42*, 5993–5996.

[29] S. Thorand, N. J. Krause, *J. Org. Chem.* **1998**, *63*, 8551–8553.

[30] A. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, *8*, 627–630.

[31] D. L. Pearson, J. M. Tour, *J. Org. Chem.* **1997**, *62*, 1376–1387.

[32] A. Belaissaoui, H. Tokuhisa, E. Koyama, M. Kanesato, *Int. J. Nanosci.* **2005**, *4*, 467–473.

[33] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985.

[34] J. M. Tour, L. R. Jones II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh, S. V. Atre, *J. Am. Chem. Soc.* **1995**, *117*, 9529–9534.

[35] Z. Bao, Y. Chen, R. Cai, L. Yu, *Macromolecules* **1993**, *26*, 5281–5286.

[36] T. Cardolaccia, A. M. Funston, M. Kose, J. M. Keller, J. R. Miller, K. S. Schanze, *J. Phys. Chem. B* **2007**, *111*, 10871–10880.

[37] T. S. Lee, H. Nakamura, T. Tsutsui, *Org. Lett.* **2001**, *3*, 2005–2007.

[38] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, Sh. Tokito, *Angew. Chem. Int. Ed.* **2003**, *42*, 1159–1162; S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S. J. Jeon, B. R. Cho, *Org. Lett.* **2005**, *7*, 323–326.

[39] P. F. H. Schwab, F. Fleischer, J. Michl, *J. Org. Chem.* **2002**, *67*, 443–449.

[40] S. I. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Gorohmaru, S. Maeda, Y. Yamashita, S. Mataka, *Chem. Commun.* **2004**, *20*, 2342–2343.

Received: July 23, 2010
Published Online: November 25, 2010

