Monodisperse Aromatic Oligomers of Defined Structure and Large Size through Selective and Sequential Suzuki Palladium-Catalyzed Cross-Coupling Reactions

Stephen Lightowler and Michael Hird*

Department of Chemistry, University of Hull, Hull, HU6 7RX, United Kingdom

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Several monodisperse aromatic oligomers of defined structure have been prepared through selective and sequential palladium-catalyzed cross-coupling reactions. The scope of the synthesis was evaluated in terms of (i) molecular size with materials ranging from relatively small sizes (5 and 6 aromatic rings) through to intermediate sizes (9 and 10 aromatic rings), right up to a monodisperse oligomer with 21 aromatic rings, and (ii) variety of molecular structure, with materials including benzene and thiophene core units, and peripheral substituents, including octyloxy, fluoro, and cyano to aid solubility and enhance polarity. The synthetic strategy involved the preparation of Grignard reagents and organolithium derivatives to generate arylboronic acids, which were then involved in selective Suzuki palladium-catalyzed cross-couplings to generate intermediate bromides. These intermediates were either converted into boronic acids and then used in further couplings or used directly in further couplings. The scope and limitations of the synthetic methodology are reported in terms of the size and variety of structure.

Introduction

The synthesis of large rodlike monodisperse oligophenylenes of defined structure has attracted much attention because of their potential use in molecular electronics, as units for stiffening main chains in semiflexible polyesters and polyimides, and as specialized standards for GPC measurements of rigid rodlike polymers.[1−4] Additionally, other monodisperse macromolecular oligomeric compounds have been synthesized based on thiophene, phenylethynylenes, and thiopheneethynylenes with a wide variety of structural types including rodlike, dendritic-like, and also macrocyclic systems.[1,5−16] However, in addition to the needs of applications, the establishment of methodologies for such syntheses is essential, not only to further increase the size of such oligomers but also to broaden the structural types of oligoarenes in general, so as to be able to tailor the structure and size to satisfy particular properties.

The most successful approaches to the synthesis of oligoarenes of defined structure have used Suzuki-type palladium-catalyzed cross-coupling reactions.[2,4,9,16] The Suzuki reaction[17,18] involves the cross-coupling of an arylboronic acid to an aryl unit that contains a leaving group (e.g., chloro, bromo, iodo, or triflate) in the presence of a palladium catalyst to generate an unsymmetrical, or symmetrical, biaryl compound.

Suzuki coupling methodologies are now employed extensively in many areas of synthetic chemistry. Liquid crystalline materials have been the subject of intense research over the past 30 years, largely due to their technological importance in displays (LCDs). Most liquid crystal materials consist of rodlike molecules, and most of these involve multiaryl structures which lend themselves perfectly to synthesis through palladium-catalyzed cross-coupling reactions, and many such materials have been generated through the Suzuki cross-coupling methodology.[19−26] Similarly, materials tar-

* To whom correspondence should be addressed. E-mail: m.hird@hull.ac.uk.

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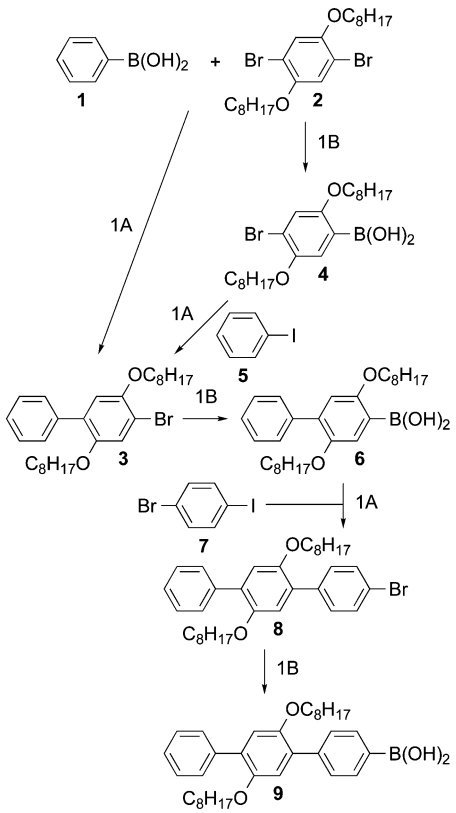
geted for the wide variety of molecular electronics applications also have multi-aryl structures, including many aromatic polymers,[1,27−34] and Suzuki couplings have been widely used in such syntheses. Suzuki couplings also find widespread use in the synthesis of natural products[35] and pharmaceuticals,[36] and further extended in the latter area to include the development of combinatorial and parallel synthesis methodologies.[37]

The use of selective Suzuki coupling reactions, first employed in the synthesis of liquid crystals,[19] greatly extends the scope and versatility of the methodology to enable the construction of large and elaborate molecules. In particular, strategies involving selective Suzuki couplings are well-suited toward the synthesis of oligophenylenes. Galda and Rehahn developed a strategy involving selective Suzuki couplings which generated oligophenylenes of up to 15 rings in size and showed that although solubility was a problem, larger sizes may be achievable if sufficient solubilizing side chains were present.[2] Liess, Hensel, and Schluter adopted a similar approach and synthesized an oligophenylene of 16 rings in size.[4] More recently, Jo et al. reported the synthesis of 7 linearly-linked fluorenes, which for comparison of size is equivalent to an oligophenylene of 14 rings.[9]

Aims and Objectives

Recently, we reported the use of the Suzuki palladium-catalyzed cross-coupling methodology in the synthesis of a wide range of novel aromatic polymers.[34] Although interesting results were obtained, we found that achievable molecular weights were rather limited to a maximum of around 80 aromatic rings. Additionally, their structural variation was necessarily restricted to the repeating unit(s) of the monomer(s), and polymers are disadvantaged by being polydisperse, and hence difficult to characterize and reproduce precisely. Accordingly, our attention turned to the synthesis of novel aromatic oligomers, and macromolecular systems in general, of defined structure which could be widely varied, in principle to the point where every ring is different. Such materials would be pure, and their structure−property relationships could then be reliably analyzed. The aim of this research was to assess the scope and limitations of a strategy involving selective and sequential Suzuki palladium-catalyzed cross-coupling reactions in the synthesis of such macromolecular structures. In particular, it was essential to investigate (i) the size to which it is possible to generate the oligomers of defined structure, (ii) the variations of structure which are possible in terms of different ring types and attached functional groups, and (iii) the degree of difficulty of purification required at each step.

Scheme 1



1A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
1B ... (i) n-BuLi, THF (ii) $(MeO)_3B$, THF (iii) 10% HCl

Benzene rings were targeted since they are extremely common aromatic units with many intermediates readily available, and thiophene rings were also investigated since they are important constituents in materials for molecular electronics. The final products were designed to investigate the synthetic methodology and not to satisfy any particular application.

The strategy of sequentially adding one ring at a time was ruled out as far too time-consuming, particularly in terms of the necessary purification at each synthetic step. Hence, a more convergent approach was taken that involved the synthesis of multi-ring sections, which were then involved in the construction of macromolecular intermediates, and ultimately final products.

Discussion

Initially, the synthesis of vital intermediates was undertaken in terms of appropriate bromides and boronic acids. Compound **9** (Scheme 1) is a valuable 3-ring boronic acid for end-capping of the wide range of macromolecular

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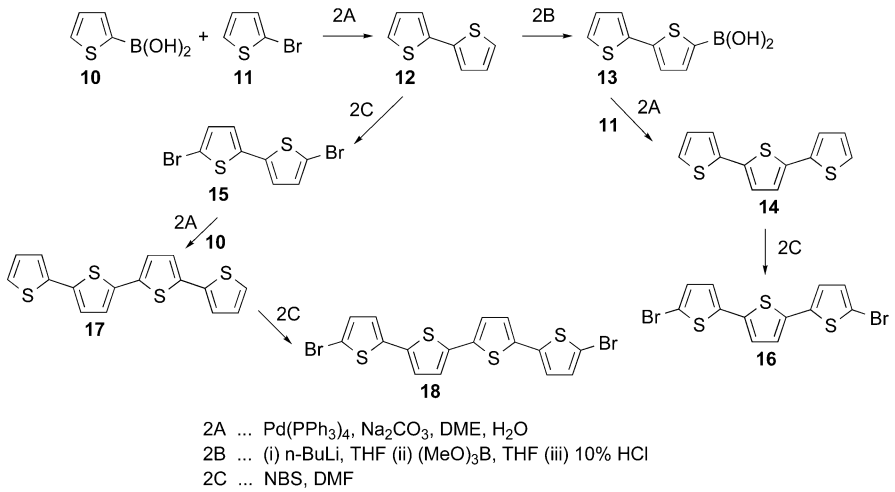
Scheme 2



dibromides in various double Suzuki coupling reactions to extend the chain by six phenyl rings.

As outlined in Scheme 1, two approaches were taken in the synthesis of the bromobiphenyl (compound **3**); both involved selective couplings to leave a bromo substituent for further functionalization. The first approach was the most simple and involved phenylboronic acid **1** in a selective Suzuki coupling with the known[34] dibromodioctyloxybenzene (**2**). It was expected that such a coupling would not be very selective since both leaving groups are identical. However, although competitive double coupling did occur to a small extent (~20% by GC-MS), purification was very straightforward, and the desired monocoupled product (compound **3**) was isolated in moderate yield (54%) after column chromatography and recrystallization. Nevertheless, this simple bromobiphenyl unit is a valuable intermediate, and so a higher yield was hoped for by using a second approach in which the two leaving groups were different. The bromophenylboronic acid (compound **4**) was generated in high yield (82%) through the monolithiation of dibromide **2**. This boronic acid was found to couple to the iodo site of compound **5**, in preference to coupling with the bromo site of the same compound, with a high degree of selectivity, resulting in a 72% isolated yield. Bromobiphenyl **3** was then converted into the boronic acid (compound **6**), which was then involved in a selective Suzuki coupling with 1-bromo-4-iodobenzene (**7**). As expected, selectivity was very much in favor of the iodo site, and a 67% yield of the desired bromoterphenyl (compound **8**) was isolated. An excess of compound **7** was used to minimize double coupling, and the excess was easily removed during purification by column chromatography. The desired terphenylylboronic acid **9** was generated from the bromide **8** via the lithium salt generated through a bromo-lithium exchange at low temperature; solubility of the terphenyl substrate was poor, which necessitated the use of a large amount of dry solvent.

Scheme 2 shows the synthesis of a range of multithiophene intermediates, namely, dibromobithiophene (**15**), dibromoterthiophene (**16**), and dibromoquaterthiophene (**18**); all were synthesized efficiently through sequential routes starting from thiophene-2-boronic acid (**10**) and 2-bromothiophene (**11**). Thiopheneboronic acids (e.g., compounds **10** and **13**) are rather prone to hydrodeboronation;[38] however, in each case, the use of a 20% excess of such boronic acids was sufficient to consume all the starting bromide, and purification of the coupled products was relatively simple. Selective dibromination of the parent oligothiophenes (e.g., compounds **12**, **14**, and **17**) in the two alpha-positions is not as simple as it would appear. *N*-Bromosuccinimide (NBS) is an excellent reagent; however, the conditions are crucial for a successful outcome. Bromination using a double excess of NBS in chlorinated solvents is not very selective and generates mixed products of di- and tribromo- analogues which are difficult to separate.[39] However, the use of DMF as the solvent is reported to be very selective;[13] hence, these conditions were used to good effect here.

Scheme 3 shows the synthesis of two smaller variants of multiphenylene oligomers (**20** and **21**). Compound **20** is only a five-ring system and was the simple product of a double Suzuki coupling of the readily available diboronic acid **19** with the bromobiphenyl **3**, but nevertheless is functionalized with solubilizing octyloxy chains. Compound **21** represents a further extension of the repeat unit from compound **20** to seven rings which was generated by a double Suzuki coupling of the known dibromo-dioctyloxybenzene **2** with the end-capping 3-ring boronic acid **9**. The yields of both compounds **20** and **21** are low by the usual standards of reported Suzuki couplings, but given the rigorous column chromatography and recrystallization purification, 41% and 51% respectively can be considered very good yields.

Scheme 4 takes the size of the oligophenylenes further, but the chemistry is less simple since more selective coupling reactions are required. Ideally, for selective couplings, two different leaving groups should be used, for example, a bromide and an iodide. However, the generation of such intermediates would have involved more steps, and although it would have been easy to convert compound **2** into a bromo-iodo analogue, the approach would have been extremely difficult for the later, more complex dibromides (e.g., **25**, **27**, **29**, Schemes 5 and 6). Hence, we decided to evaluate

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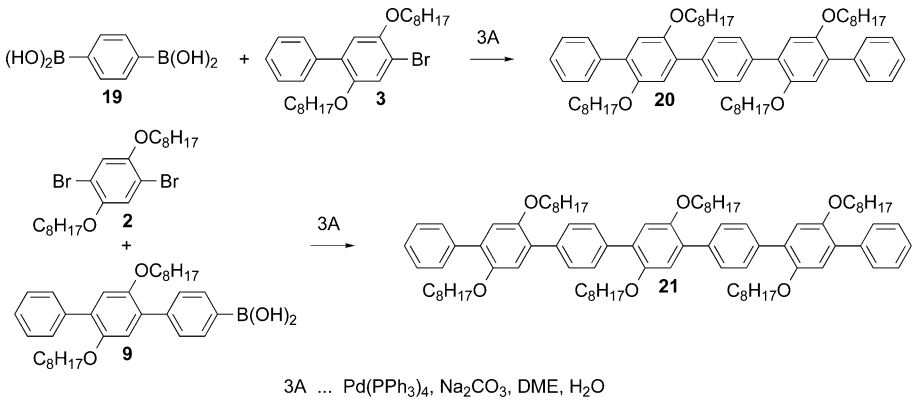
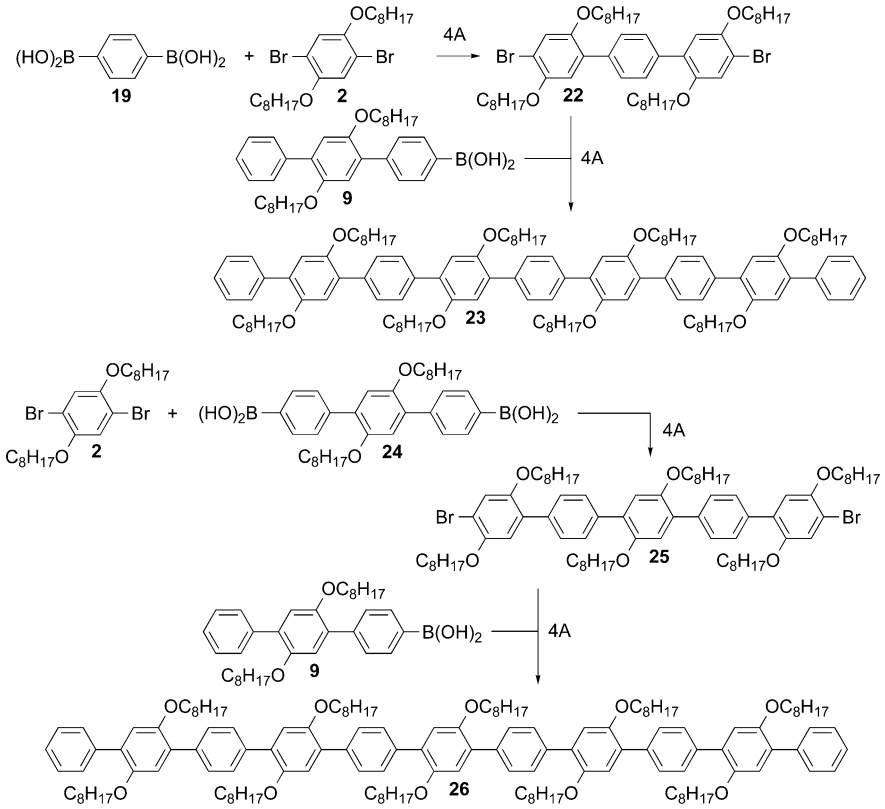
Scheme 3



3A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O

Scheme 4

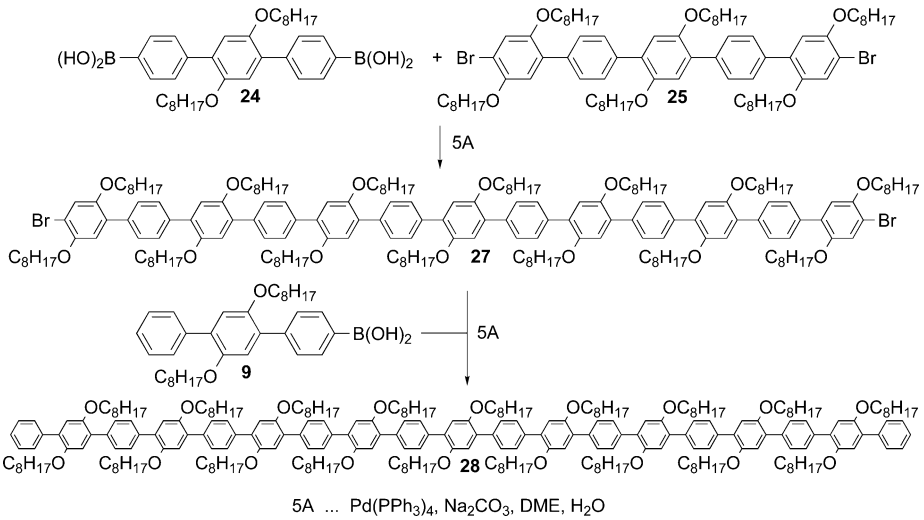


4A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O

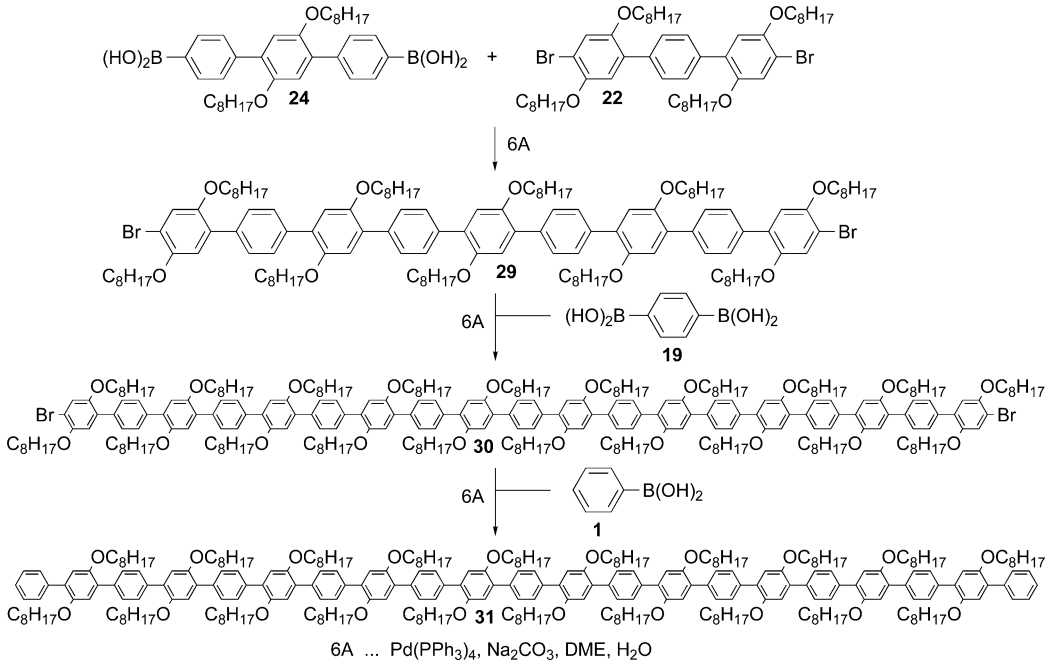
the scope of the most crude selectivity in Suzuki couplings to synthesize large oligomers without the need for additional synthetic steps. A large excess of the dibromide **2** was employed in the reaction with diboronic acid **19** to help ensure a reasonable preference for the formation of compound **22** and minimize polymerization. In the event, the degree of success in generating compound **22** was rather surprising, and although the isolated yield was just 24%, the purification was relatively simple. The 3-ring dibromide was then double-coupled with the end-capping 3-ring boronic acid **9** to generate the 9-ring oligomeric phenylene (**23**) in 45% yield. The capability of the simple selective coupling strategy was taken further with the selective coupling of dibromide **2** with the larger, 3-ring diboronic acid **24** which was available from our previous work[34] involving polymerizations of dibromides and diboronic acids. Selectivity here in generating the 5-ring dibromide product (**25**) was again seemingly quite poor with a 22% isolated yield, but given the relative ease of purification, the synthetic strategy is working well. Once again, a final double Suzuki coupling, this time with the 5-ring dibromide (**25**) and the 3-ring end-capping boronic acid **9,** generated an 11-ring oligophenylene (**26**) in identical isolated yield (45%) to compound **23**.

In a further extension of the synthetic strategy, the 5-ring dibromooligophenylene **25** was doubly coupled to the 3-ring double boronic acid **24** to give the 13-ring intermediate dibromide **27** (Scheme 5) in the same style as compound **25** was originally generated (Scheme 4). Surprisingly, the larger dibromide (**27**) was generated in higher yield than the smaller analogue (**25**), probably due to the reduced solubility of compound **27** limiting further coupling reactions. The 13-ring dibromide (**27**) was then doubly end-capped through

Scheme 5



Scheme 6

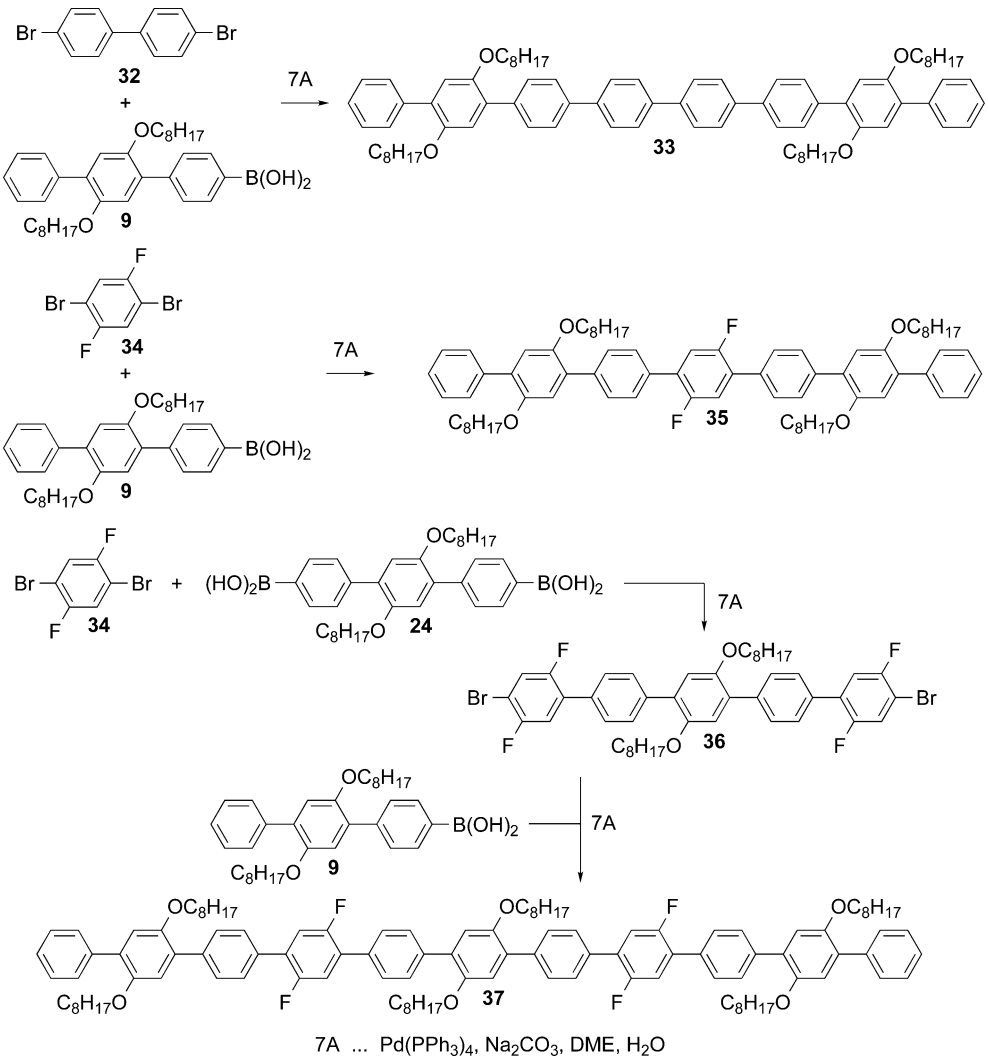


coupling to the 3-ring boronic acid (**9**) to generate a 19-ring oligophenylene (**28**) in 50% yield, consistent with that achieved for the smaller final oligomers.

It was hoped to be able to extend the systems further, but diminishing quantities dictated that all available **27** was used in generating compound **28**. Nevertheless, we did want to generate larger oligophenylenes, and compounds **2** and **19** were available in large quantity, so compound **22** was prepared as described in the Experimental Section, except on a very large scale, generating 8.55 g (19%). Nevertheless, our strategy of selective coupling which involved using a 4 times excess of the dibromooligophenylenes (e.g., compounds **2**, **22**, and **25**) to ensure optimum product yields was consuming very large quantities. Hence, in the synthesis of compound **29** a rather conservative 2.7 times excess of the dibromooligophenylene **22** was used, and in fact the yield (29%) was very similar to those cases where a 4 times excess of the dibromide was being used. A further selective coupling was going to be necessary if a longer oligophenylene was to be generated. The simple single-ring double boronic acid (**19**) was chosen to selectively couple with the 9-ring dibromooligophenylene (**29**), and despite the use of just a 2.5 times excess of the double bromide, a surprisingly high yield (48%) of the 19-ring dibromide (**30**) was isolated. The 19-ring dibromide was then doubly end-capped with a large excess (5 times) of phenylboronic acid (**1**), which resulted in a 55% yield of the desired 21-ring oligophenylene (**31**).

Thus far, solubility was not a serious problem, probably due to the large number of solubilizing lateral octyloxy chains, and hence further extensions would have been possible, but sufficient quantities of intermediate were not available. Given the many steps and the relatively low yields, the reactions would need to be optimized somewhat before embarking on any extension of the 21-ring compound **31** which is believed to be the largest such linear system reported. Much larger systems of the dendritic type have been reported,[11,12,15] but these systems do have a great many more reaction sites than just the two for linear systems.

Scheme 7



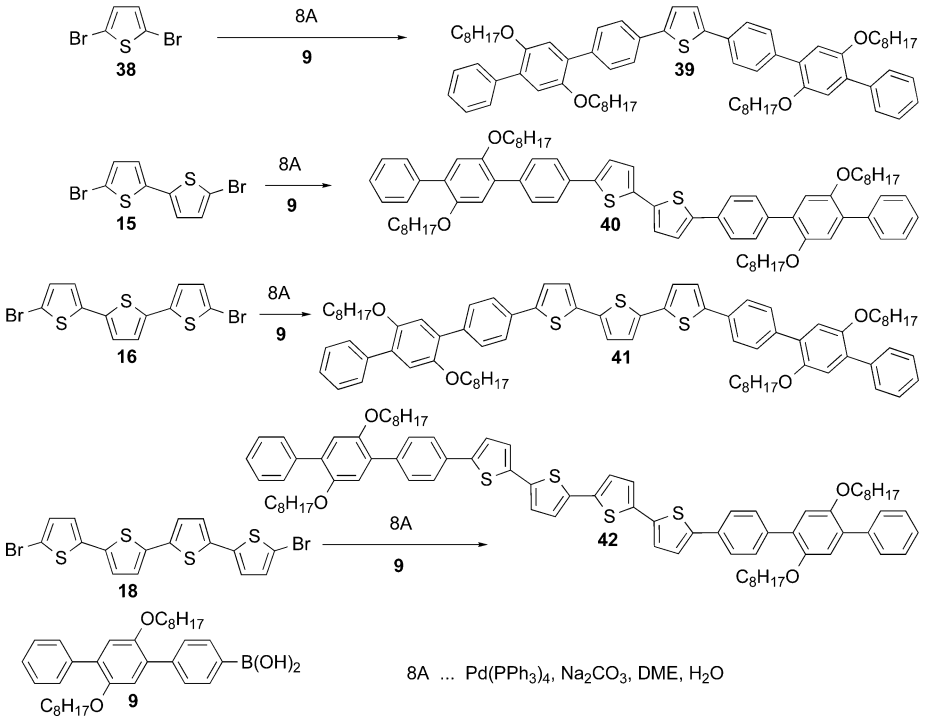
7A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O

The remaining synthetic schemes are not particularly concerned with size, but rather aimed at illustrating the structural variety possible from the synthetic strategy. Scheme 7 shows the simple end-capping of commercially available dibromobiphenyl (**32**) and dibromo-difluorobenzene (**34**) with the 3-ring boronic acid (**9**) to give compounds **33** and **35** respectively in yields of around 50%. Not surprisingly, given the rodlike molecular architecture, compound **33** is liquid crystalline and melts to a nematic phase at 225 °C and clears to the isotropic liquid at 298 °C. What is perhaps surprising is that none of the (much) longer oligophenylenes (e.g., **23**, **26**, **28**, and **31**) exhibit liquid crystalline phases. However, these compounds all have alternating rings substituted with long lateral solubilizing octyloxy chains, which prevent mesomorphism, despite all having much lower melting points than compound **33**.

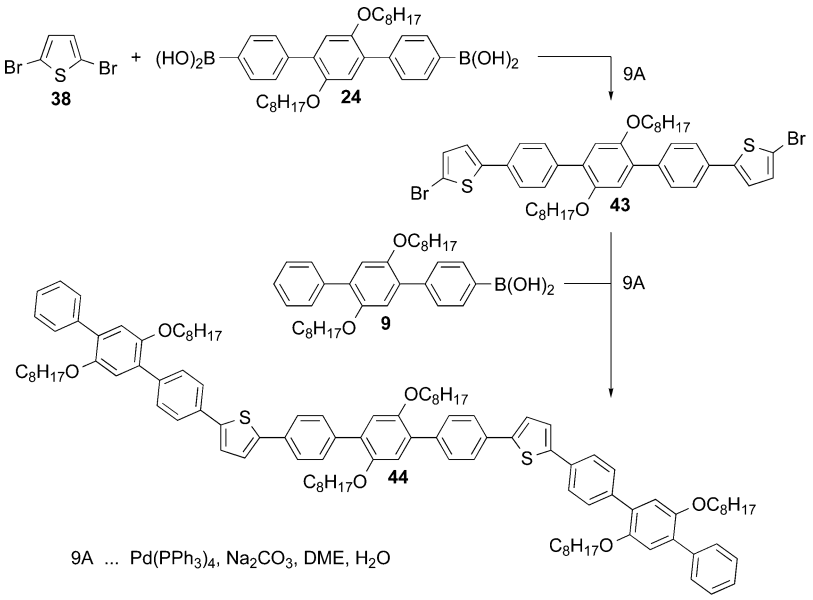
Dibromodifluorobenzene (**34**) was extended through the selective coupling strategy to generate a 5-ring dibromoquinquephenyl of tailored structure (**36**); however, the yield of 53% is significantly higher than that for the previous such examples discussed above, perhaps due to the smaller size of the fluoro substituents when compared with that of the octyloxy chains. The double end-capping of compound **36** with the 3-ring boronic acid (**9**) generated an 11-ring compound (**37**) with fluoro and octyloxy substituents in 44% yield. Clearly, further functionalization of the dibromo compound (**36**) with other substituted phenylene systems could provide wide variations in structure, but limited quantities of materials precluded such attempts at this stage.

Oligothiophenes have been targeted as electrically conducting organic materials for a variety of applications such as organic transistors.[1,14,16] Hence, it was thought useful to incorporate oligothiophene sections into the current synthetic strategy. Scheme 8 shows respectively the end-capping of 1-, 2-, 3-, and 4-ring dibromothiophenes (see Scheme 2) with the 3-ring boronic acid (**9**) to give compounds **39**−**42** in similar yields of around 45%. Interestingly, the melting points of compounds **39**−**42** show an "odd−even" effect, in that the angular nature of compound **39** dictates a low melting point (60 °C), actually remarkably low for a 7-ring compound; yet two thiophene rings (compound **40**) permit a more linear structure which improves molecular packing, and hence a higher melting point of 135 °C. On going to three thiophene rings (compound **41**) a bent structure returns, which disrupts molecular packing and confers a lower melting point of 121 °C; however, compound **42** with four thiophene rings can adopt a more linear shape, and hence has a much higher melting point of 159 °C. Scheme 8 shows once again the wide structural variation offered by the synthetic strategy.

Scheme 8



Scheme 9

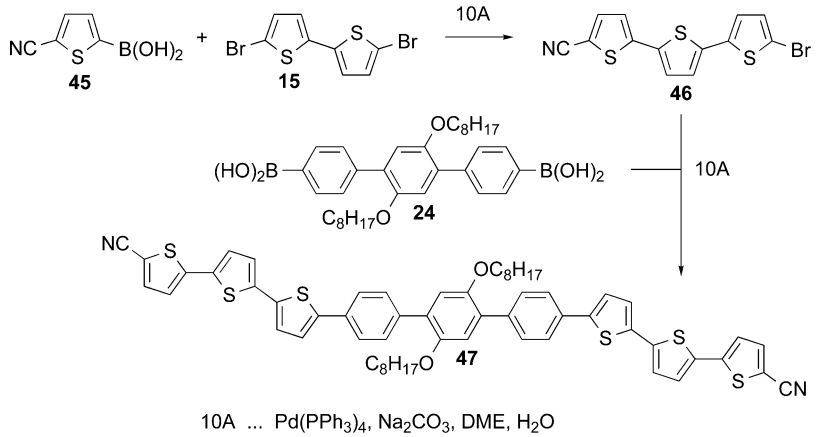


Scheme 9 illustrates a selective coupling between the 3-ring boronic acid **24** with 2,5-dibromothiophene (**38**) which provided a 5-ring dibromo intermediate with two thiophene rings (**43**) in 21% yield, which is typical for such selective couplings. Subsequent double end-capping of compound **43** with the 3-ring boronic acid generated a 64% yield of the 11-ring macromolecular system **44**. Interestingly, the melting point of compound **44** is only 71 °C, which is remarkably low for an 11-ring compound; compounds **26** and **37** are also 11-ring compounds, but without thiophene rings, and melting points are 170 and 158 °C, respectively.

Scheme 10 shows a further variety of structure for multi-ring compounds. A selective coupling of dibromobithiophene **15** with the cyanothiopheneboronic acid **45** generated the bromocyanoterthiophene intermediate **46** in moderate yield (35%). The 3-ring diboronic acid **23** was doubly end-capped with intermediate **46** to give the desired 9-ring macromolecule with two terminal cyano groups (compound **47**). Terminal cyano aromatic compounds of a rodlike molecular architecture tend to generate liquid crystal phases, so it is no surprise that compound **47** exhibits a nematic phase, melting at 204 °C and clearing at 343 °C.

Particular comments are required with respect to the yields and the purification of the intermediates and final products. Rigorous purification was undertaken at each step by slow and careful column chromatography, followed by recrystallization. Just as solubility was enhanced by the many solubilizing octyloxy chains, purification was facilitated by their presence by making the desired product sufficiently different from the starting materials and other possible

Scheme 10



products to enable chromatographic separation. In many cases the yields may seem rather low; however, given selectivity issues, the purification process, and losses in recrystallizations, they could most certainly be considerably improved.

Conclusions

The synthetic strategy has led to the synthesis of a wide range of very large macromolecules which, unlike polyphenylenes, are pure materials of defined structure. In dendritic structures, many larger systems have been prepared, but no structural variation has been attempted.[11,12,15] Also, the nature of the dendritic structure facilitates the synthesis of larger systems because there are many more points of attachment than for linear macromolecules. In terms of linearly linked oligophenylenes, the 21-ring unit reported here is, to the best of our knowledge, the largest reported. However, it is not simply the size of the system, but the applicability of the synthetic strategy to develop a wide range of tailored structures, including different ring types, and rings containing a wide variety of lateral substituents, thus enabling desirable physical properties to be more readily achieved.

Experimental Section

Structural information of materials was obtained, where appropriate, by ^{1}H and ^{13}C NMR spectroscopy (JEOL Eclipse 400 MHz spectrometer), and by mass spectrometry (Finnigan-MAT 1020 spectrometer for low relative molecular mass intermediates, and Bruker Reflex IV MALDI-TOF for high relative molecular mass intermediates and all final compounds, using 2-(4-hydroxyphenylazo)benzoic acid as matrix). The progress of some reactions, and the purity of certain materials, was analyzed by gas liquid chromatography (GLC) using a Chrompack CP-9001 gas chromatograph with a 10 m, 0.25 mm internal diameter, 0.12 mm fused silica capillary column. Melting points and transition temperatures were determined using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 temperature controller, and in the case of final compounds these values were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station). Elemental analysis (Fisons EA1108 CHN) data were obtained for the final compounds (**20**, **21**, **23**, **26**, **28**, **31**, **33**, **35**, **37**, **39**−**42**, **44**, and **47**), and the purity of each was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were found to be >99% pure in each case.

Although the boronic acids prepared (**4**, **6**, **9**, and **13**) were undoubtedly the usual mixture of boronic acid and the anhydride, the NMR spectra were determined in deuterated-DMSO, which has a sufficient water content to ensure that solely boronic acid is analyzed. Melting points of boronic acids could be unreliable because of the presence of unknown varying amounts of anhydride.

Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure,[40] compounds **2**, **19**, and **24** were prepared according to the literature procedures,[34] and compounds **1**, **5**, **7**, **10**, **11**, **32**, **34**, **38**, and **45** are all commercially available.

Nomenclature of multi-aryl systems can become tedious and extremely lengthy because of the number of primes required to define each ring. Consequently, in this paper the number of primes has been indicated with a superscript number for compounds that constitute 5-ring molecular structures and higher.

4-Bromo-2,5-dioctyloxybiphenyl (3)—Method 1. Tetrakis(triphenylphosphine)palladium(0) (0.2513 g, 0.217 mmol) was added in one portion to a stirred, degassed mixture of compound **2** (10.00 g, 0.020 mol), sodium carbonate (6.00 g), 1,2-dimethoxyethane (40 mL), and water (60 mL) under dry nitrogen. The mixture was heated under reflux, and a solution of compound **1** (2.73 g, 0.022 mol) in 1,2-dimethoxyethane (40 mL) was added dropwise. The mixture was heated under reflux overnight (GLC and TLC analyses revealed a complete reaction) and cooled. Water was added, and the crude product was extracted into ether (twice). The combined ethereal extracts were washed with brine and dried ($MgSO_4$). The desiccant was filtered off, the solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel/hexane with the gradual introduction of dichloromethane) to give a colorless solid which was crystallized from ethanol to yield colorless crystals.

Yield: 5.33 g (54%). mp: 32 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.70 (2H, quint), 1.80 (2H, quint), 3.86 (2H, t), 3.99 (2H, t), 6.90 (1H, s), 7.15 (1H, s), 7.32 (1H, t), 7.40 (2H, t), 7.50 (2H, dd). MS (*m*/*z*): 490 (M^+), 488 (M^+).

4-Bromo-2,5-dioctyloxyphenylboronic Acid (4). A solution of *n*-butyllithium (23 mL, 2.5 M in hexane, 0.058 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound **2** (25.00 g, 0.051 mol) in dry THF (300 mL) under an atmosphere of dry nitrogen. The reaction mixture was stirred at −78 °C for 1 h (GLC analysis revealed a complete reaction). A solution of trimethyl borate (10 g, 0.1 mol) in dry THF (50 mL) was added dropwise at −78 °C, and the mixture was allowed to attain room temperature overnight. 10% hydrochloric acid (300 mL) was added, and the product was extracted into ether (twice). The combined ether layers were washed with water, dried ($MgSO_4$), and filtered

(40) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121−124.

and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel/dichloromethane with the gradual introduction of ethyl acetate) to give a colorless solid.

Yield: 19.10 g (82%). mp: 120−125 °C (see note in Experimental Section). ^{1}H NMR (DMSO): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.80 (4H, quint), 3.90 (4H, 2xt), 6.90 (1H, s), 7.35 (1H, s), 8.10 (2H, s). MS (*m*/*z*): 458 (M^+), 456 (M^+).

4-Bromo-2,5-dioctyloxybiphenyl (3)—Method 2. Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.4260 g, 0.369 mmol), compound **5** (13.70 g, 0.067 mol), and compound **4** (15.31 g, 0.034 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to yield colorless crystals.

Yield: 11.95 g (72%). See Method 1 for compound characterization data.

2,5-Dioctyloxybiphenyl-4-ylboronic acid (6). Quantities were as follows: compound **3** (25 g, 0.051 mol) in dry THF (500 mL) and *n*-butyllithium (23 mL, 2.5 M in hexane, 0.058 mol). The experimental procedure was as described for the preparation of compound **4** to yield a colorless solid.

Yield: 18.10 g (78%). mp: 191−194 °C (see note in Experimental Section). ^{1}H NMR (DMSO): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.80 (4H, quint), 3.86 (2H, t), 3.90 (4H, 2xt), 6.90 (1H, s), 7.35 (1H, s), 7.32 (1H, t), 7.40 (2H, t), 7.50 (2H, dd), 8.10 (2H, s). MS (*m*/*z*): 454 (M^+).

4-Bromo-2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl (8). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.4428 g, 0.383 mmol), compound **7** (9.90 g, 0.035 mol), and compound **6** (16.00 g, 0.035 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid that was crystallized from ethanol-ethyl acetate (9:1) to yield colorless crystals.

Yield: 13.22 g (67%). mp: 62 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.70 (4H, quint), 3.90 (4H, 2xt), 6.93 (1H, s), 6.97 (1H, s), 7.35 (1H, t), 7.40 (2H, t), 7.50 (4H, 2xd), 7.58 (2H, d). MS (*m*/*z*): 566 (M^+), 564 (M^+).

2′,5′-Dioctyloxy-1,1′:4′,1″-terphenyl-4-ylboronic Acid (9). Quantities were as follows: compound **8** (12.50 g, 0.022 mol) in dry THF (1200 mL) and *n*-butyllithium (10 mL, 2.5 M in hexane, 0.025 mol). The experimental procedure was as described for the preparation of compound **4** to yield a colorless solid.

Yield: 8.20 g (70%). mp: 216−220 °C (see note in Experimental Section). ^{1}H NMR (DMSO): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.80 (4H, quint), 3.90 (4H, 2xt), 6.93 (1H, s), 6.97 (1H, s), 7.35 (1H, t), 7.40 (2H, t), 7.50 (4H, 2xd), 7.88 (2H, d), 8.05 (2H, s). MS (*m*/*z*): 530 (M^+).

2,2′-Bithiophene (12). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (1.80 g, 1.56 mmol), compound **11** (25.00 g, 0.153 mol), and compound **10** (24.50 g, 0.191 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1). The crude product was purified by column chromatography (silica gel/hexane) to give a pale green solid which was crystallized from ethanol to yield pale green tinted crystals.

Yield: 17.20 g (68%). mp: 33 °C (lit. mp = 33 °C).[13] ^{1}H NMR ($CDCl_3$): δ 7.06 (2H, dd, J = 3.3 Hz, J = 2.3 Hz), 7.20 (2H, dd, J = 2.3 Hz, J = 1 Hz), 7.22 (2H, dd, J = 3.2 Hz, J = 1 Hz). MS (*m*/*z*): 166 (M^+).

2,2′-Bithiophene-5-boronic Acid (13). Quantities were as follows: compound **12** (7.00 g, 0.042 mol) in dry THF (200 mL) and *n*-butyllithium (18 mL, 2.5 M in hexane, 0.045 mol). The experimental procedure was as described for the preparation of compound **4** to yield a colorless solid.

Yield: 6.40 g (73%). mp: 92−95 °C (see note in Experimental Section). ^{1}H NMR ($CDCl_3$): δ 7.05 (1H, dd, J = 2.5 Hz, J = 2.5 Hz), 7.26−7.32 (3H, m), 7.58 (1H, d, J = 2.5 Hz). MS (*m*/*z*): 210 (M^+).

2,2′:5′,2″-Terthiophene (14). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.3013 g, 0.261 mmol), compound **11** (3.90 g, 0.024 mol), and compound **13** (6.30 g, 0.030 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a pale yellow solid which was crystallized from ethanol-ethyl acetate (9:1) to yield pale yellow tinted crystals.

Yield: 3.58 g (60%). mp: 95 °C (lit. mp = 95 °C).[13] ^{1}H NMR ($CDCl_3$): δ 7.00−7.25 (m). MS (*m*/*z*): 248 (M^+).

5,5′-Dibromo-2,2′-bithiophene (15). *N*-Bromosuccinimide (19.50 g, 0.110 mol) was added portion-wise to a stirred solution of compound **12** (9.00 g, 0.054 mol) in dry DMF (100 mL) at room temperature. The mixture was stirred overnight and poured onto ice−water. The product was filtered off, washed with lots of water, and dried (P_2O_5). The crude product was recrystallized from ethanol-ethyl acetate (9:1) to yield colorless crystals.

Yield: 13.80 g (79%). mp: 146 °C (lit. mp = 146 °C).[13] ^{1}H NMR ($CDCl_3$): δ 6.85 (2H, d, J = 3.5 Hz), 6.96 (2H, d, J = 3.5 Hz). MS (*m*/*z*): 326 (M^+), 324 (M^+), 322 (M^+).

5,5′-Dibromo-2,2′:5′,2″-terthiophene (16). Quantities were as follows: *N*-bromosuccinimide (5.00 g, 0.028 mol) and compound **14** (3.40 g, 0.014 mol). The experimental procedure was as described for the preparation of compound **15**. The crude product was recrystallized from ethanol-ethyl acetate (1:1) to yield yellow crystals.

Yield: 4.10 g (72%). mp: 160 °C (lit. mp = 160 °C).[13] ^{1}H NMR ($CDCl_3$): δ 6.90 (2H, d, J = 3.8 Hz), 6.96 (2H, d, J = 3.8 Hz), 6.98 (1H, s). MS (*m*/*z*): 408 (M^+), 406 (M^+), 404 (M^+).

2,2′:5′,2″:5″, 2‴-Quaterthiophene (17). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.7364 g, 0.637 mmol), compound **15** (10.00 g, 0.031 mol), and compound **10** (10.00 g, 0.078 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1). The crude product was purified by column chromatography (silica gel/hexane) to give a pale yellow solid which was crystallized from ethanol-ethyl acetate (1:1) to yield yellow tinted crystals.

Yield: 5.92 g (58%). mp: 212 °C (lit. mp = 212 °C).[13] ^{1}H NMR ($CDCl_3$): δ 7.00−7.25 (m). MS (*m*/*z*): 330 (M^+).

5,5′-Dibromo-2,2′:5′,2″:5″, 2‴-quaterthiophene (18). Quantities used were as follows: *N*-bromosuccinimide (5.00 g, 0.028 mol) and compound **17** (4.62 g, 0.014 mol). The experimental procedure was as described for the preparation of compound **15**. The crude product was recrystallized from ethyl acetate to yield an orange powder.

Yield: 4.51 g (66%). mp: 264 °C (lit. mp = 264 °C).[13] ^{1}H NMR ($CDCl_3$): δ 6.90 (2H, d, J = 3.8 Hz), 6.98 (2H, d, J = 3.8 Hz), 7.01 (2H, d, J = 3.8 Hz), 7.06 (2H, d, J = 3.8 Hz). MS (*m*/*z*): 490 (M^+), 488 (M^+), 486 (M^+).

2^1,2^3,5^1,5^3-Tetraoctyloxy-1,1^1:4^1,1^2:4^2,1^3:4^3,1^4-quinquephenyl (20). Quantities were as follows: tetrakis(triphenylphosphine)-palladium(0) (0.0563 g, 0.049 mmol), compound **3** (1.50 g, 3.07 mmol), and compound **19** (0.2504 g, 1.51 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (9:1) to yield a colorless powder.

Yield: 0.56 g (41%). mp: 126 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, t), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.70 (8H, quint), 3.93 (8H, 2xt), 7.01 (2H, s), 7.06 (2H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.67 (4H, s). MALDI-TOF MS (*m*/*z*): 895.34

(M^+). Elemental analysis: calcd for $C_{62}H_{86}O_4$: C, 83.17; H, 9.68. Found: C, 83.05; H, 9.71.

$2^1,2^3,2^5,5^1,5^3,5^5$-Hexaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$-septiphenyl (21). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0537 g, 0.046 mmol), compound **2** (0.6053 g, 1.23 mmol), and compound **9** (1.44 g, 2.71 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (9:1) to yield a colorless powder.

Yield: 0.82 g (51%). mp: 149 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.76 (12H, m), 3.96 (12H, m), 7.01 (2H, s), 7.07 (2H, s), 7.09 (2H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.69 (8H, s). MALDI-TOF MS (*m*/*z*): 1303.96 (M^+). Elemental analysis: calcd for $C_{90}H_{126}O_6$: C, 82.90; H, 9.74. Found: C, 82.84; H, 9.82.

4,4″-Dibromo-2,2″,5,5″-tetraoctyloxy-1,1′:4′,1″-terphenyl (22). Quantities were as follows: tetrakis(triphenylphosphine)palladium-(0) (0.1732 g, 0.150 mmol), compound **2** (14.25 g, 0.029 mol), and compound **19** (1.20 g, 7.23 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (9:1) to yield a colorless powder.

Yield: 1.56 g (24%). mp: 101 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, t), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.70 (4H, quint), 1.82 (4H, quint), 3.90 (4H, t), 4.01 (4H, t), 6.95 (2H, s), 7.17 (2H, s), 7.56 (4H, s). MALDI-TOF MS (*m*/*z*): 900.94 (M^+).

$2^1,2^3,2^5,2^7,5^1,5^3$$5^5$$5^7$-Octaoctyloxy-$1,1^1$:$4^1,1^2$,$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$-noviphenyl (23). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0521 g, 0.045 mmol), compound **22** (0.7510 g, 0.834 mmol), and compound **9** (1.00 g, 1.87 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a colorless powder.

Yield: 0.64 g (45%). mp: 166 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (24H, m), 1.20−1.40 (64H, m), 1.48 (16H, m), 1.76 (16H, m), 3.96 (16H, m), 7.01 (2H, s), 7.06 (2H, s), 7.11 (4H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.69 (12H, s). MALDI-TOF MS (*m*/*z*): 1712.58 (M^+). Elemental analysis: calcd for $C_{118}H_{166}O_8$: C, 82.76; H, 9.77. Found: C, 82.68; H, 9.78.

$4,4^4$-Dibromo-$2,2^2,2^4,5,5^2,5^4$-hexaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$ -quinquephenyl (25). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (0.1534 g, 0.133 mmol), compound **2** (10.30 g, 0.021 mol), and compound **24** (3.00 g, 5.23 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 1.52 g (22%). mp: 126 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.70 (8H, quint), 1.80 (4H, quint), 3.84 (4H, t), 3.88 (4H, t), 3.95 (4H, t), 6.91 (2H, s), 6.98 (2H, s), 7.11 (2H, s), 7.55 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 1309.56 (M^+).

$2^1,2^3,2^5,2^7,2^9,5^1,5^3,5^5,5^7,5^9$-Decaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$:$4^8,1^9$:$4^9,1^{10}$-undeciphenyl (26). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0545 g, 0.047 mmol), compound **25** (0.3016 g, 0.230 mmol), and compound **9** (0.2778 g, 0.524 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.22 g (45%). mp: 170 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (30H, m), 1.20−1.40 (80H, m), 1.48 (20H, m), 1.76 (20H, m), 3.96 (20H, m), 7.01 (2H, s), 7.06 (2H, s), 7.11 (6H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.69 (12H, s). MALDI-TOF MS (*m*/*z*): 2121.19 (M^+). Elemental analysis: calcd for $C_{146}H_{206}O_{10}$: C, 82.67; H, 9.79. Found: C, 82.55; H, 9.81.

$4,4^{12}$-Dibromo-$2,2^2,2^4,2^6,2^8,2^{10},2^{12},5,5^2,5^4,5^6,5^8,5^{10},5^{12}$-tetradecaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$:$4^8,1^9$:$4^{10},1^{11}$:$4^{11},1^{12}$-terdeciphenyl (27). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (0.0504 g, 0.044 mmol), compound 25 (1.15 g, 0.88 mmol), and compound 24 (0.1704 g, 0.297 mmol). The experimental procedure was as described for the preparation of compound 3 (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.28 g (32%). mp: 143 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (42H, m), 1.20−1.40 (112H, m), 1.48 (28H, m), 1.70 (24H, quint), 1.80 (4H, quint), 3.85 (20H, t), 3.90 (4H, t), 3.97 (4H, t), 6.91 (2H, s), 6.98 (2H, s), 7.11 (2H, s), 7.55 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 2944.02 (M^+).

$2^1,2^3,2^5,2^7,2^9,2^{11},2^{13},2^{15},2^{17},5^1,5^3,5^5,5^7,5^9,5^{11},5^{13},5^{15},5^{17}$-Decaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$:$4^8,1^9$:$4^9,1^{10}$:$4^{10},1^{11}$:$4^{11},1^{12}$:$4^{12},1^{13}$:$4^{13},1^{15}$:$4^{15},1^{16}$:$4^{16},1^{17}$:$4^{17},1^{18}$-undeviciphenyl (28). Quantities were as follows: tetrakis(triphenylphosphine)palladium-(0) (0.0551 g, 0.048 mmol), compound 27 (0.2510 g, 0.085 mmol), and compound 9 (0.1241 g, 0.234 mmol). The experimental procedure was as described for the preparation of compound 3 (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.16 g (50%). mp: 178 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (54H, m), 1.20−1.40 (144H, m), 1.48 (36H, m), 1.76 (36H, m), 3.96 (36H, m), 7.01 (2H, s), 7.06 (2H, s), 7.11 (14H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.69 (12H, s). MALDI-TOF MS (*m*/*z*): 3755.66 (M^+). Elemental analysis: calcd for $C_{258}H_{366}O_{18}$: C, 82.51; H, 9.82. Found: C, 82.42; H, 9.85.

$4,4^8$-Dibromo-$2,2^2,2^4,2^6,2^8,5,5^2,5^4,5^6,5^8$-tetradecaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$-noviphenyl (29). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.1043 g, 0.090 mmol), compound **22** (8.45 g, 9.38 mmol), and compound **24** (2.00 g, 3.48 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 2.15 g (29%). mp: 167 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.70 (8H, quint), 1.80 (4H, quint), 3.84 (4H, t), 3.88 (4H, t), 3.95 (4H, t), 6.91 (2H, s), 6.98 (2H, s), 7.11 (2H, s), 7.55 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 2126.79 (M^+).

$4,4^{18}$-Dibromo-$2,2^2,2^4,2^6,2^8,2^{10},2^{12},2^{14},2^{16},2^{18},5,5^2,5^4,5^6,5^8,5^{10},5^{12},5^{14},5^{16},5^{18}$-didecaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$:$4^8,1^9$:$4^9,1^{10}$:$4^{10},1^{11}$:$4^{11},1^{12}$:$4^{12},1^{13}$:$4^{13},1^{15}$:$4^{15},1^{16}$:$4^{16},1^{17}$:$4^{17},1^{18}$-undeviciphenyl (30). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (0.0529 g, 0.046 mmol), compound 29 (2.05 g, 0.96 mmol), and compound 19 (0.0652 g, 0.393 mmol). The experimental procedure was as described for the preparation of compound 3 (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.78 g (48%). mp: 193 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.70 (8H, quint), 1.80 (4H, quint), 3.84 (4H, t), 3.88 (4H, t), 3.95 (4H, t), 6.91 (2H, s), 6.98 (2H, s), 7.11 (2H, s), 7.55 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 4169.87 (M^+).

$2^1,2^3,2^5,2^7,2^9,2^{11},2^{13}2^{15},2^{17},2^{19},5^1,5^3,5^5,5^7,5^9,5^{11},5^{13},5^{15},5^{17},5^{19}$-Didecaoctyloxy-$1,1^1$:$4^1,1^2$:$4^2,1^3$:$4^3,1^4$:$4^4,1^5$:$4^5,1^6$:$4^6,1^7$:$4^7,1^8$:$4^8,1^9$:$4^9,1^{10}$:$4^{10},1^{11}$:$4^{11},1^{12}$:$4^{12},1^{13}$:$4^{13},1^{15}$:$4^{15},1^{16}$:$4^{16},1^{17}$:$4^{17},1^{18}$:$4^{18},1^{19}$:$4^{19},1^{19}$:$4^{19},1^{20}$-semeletviciphenyl (31). Quantities were as

follows: tetrakis(triphenylphosphine)palladium(0) (0.0515 g, 0.045 mmol), compound 30 (0.6514 g, 0.156 mmol), and compound 1 (0.1036 g, 0.849 mmol). The experimental procedure was as described for the preparation of compound 3 (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.36 g (55%). mp: 178 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (54H, m), 1.20−1.40 (144H, m), 1.48 (36H, m), 1.76 (36H, m), 3.96 (36H, m), 7.01 (2H, s), 7.06 (2H, s), 7.11 (14H, s), 7.33 (2H, t), 7.42 (4H, t), 7.63 (4H, dd), 7.69 (12H, s). MALDI-TOF MS (*m*/*z*): 4164.27 (M^+). Elemental analysis: calcd for $C_{286}H_{406}O_{20}$: C, 82.49; H, 9.83. Found: C, 82.40; H, 9.89.

2^1,2^6,5^1,5^6-Tetraoctyloxy-1,1^1:4^1,1^2:4^2,1^3:4^3,1^4:4^4,1^5:4^5,1^6:4^6,1^7-octiphenyl (33). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0548 g, 0.047 mmol), compound **32** (0.4008 g, 1.28 mmol), and compound **9** (1.50 g, 2.83 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a colorless powder.

Yield: 0.75 g (52%). Transitions (°C): Cryst 225 N 298 Iso. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, m), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.70 (8H, m), 3.96−4.00 (8H, m), 7.06 (4H, s), 7.50−7.54 (4H, m), 7.58−7.61 (4H, m), 7.64−7.68 (4H, m), 7.71−7.77 (14H, m). MALDI-TOF MS (*m*/*z*): 1123.63 (M^+). Elemental analysis: calcd for $C_{80}H_{98}O_4$: C, 85.51; H, 8.79. Found: C, 85.42; H, 8.87.

2^3,5^3-Difluoro-2^1,2^5,5^1,5^5-tetraoctyloxy-1,1^1:4^1,1^2:4^2,1^3:4^3,1^4:4^4,1^5:4^5,1^6-septiphenyl (35). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0503 g, 0.044 mmol), compound **34** (0.3510 g, 1.29 mmol), and compound **9** (1.50 g, 2.83 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (9:1) to yield a colorless powder.

Yield: 0.67 g (48%). mp: 119 °C. ^{1}H NMR ($CDCl_3$): δ 0.86 (6H, t), 0.88 (6H, t), 1.20−1.40 (40H, m), 1.69 (4H, quint), 1.73 (4H, quint), 3.93 (4H, t), 3.96 (4H, t), 7.02 (2H, s), 7.05 (2H, s), 7.30−7.40 (4H, m), 7.43 (4H, t), 7.62 (4H, dd), 7.67 (4H, d), 7.73 (4H, d). MALDI-TOF MS (*m*/*z*): 1083.52 (M^+). Elemental analysis: calcd for $C_{74}H_{92}F_2O_4$: C, 82.03; H, 8.56. Found: C, 81.89; H, 8.66.

4,4^4-Dibromo-2,2^4,5,5^4-tetrafluoro-2^2,5^2-dioctyloxy-1,1^1:4^1,1^2:4^2,1^3:4^3,1^4-quinquephenyl (36). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0582 g, 0.050 mmol), compound **34** (2.30 g, 8.46 mmol), and compound **24** (1.20 g, 2.09 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a colorless solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a colorless powder.

Yield: 0.96 g (53%). mp: 106 °C. ^{1}H NMR ($CDCl_3$): δ 0.85 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.72 (4H, quint), 3.96 (4H, t), 7.04 (2H, s), 7.27−7.32 (2H, m), 7.38−7.42 (2H, m), 7.56−7.62 (4H, m), 7.71 (4H, d). MALDI-TOF MS (*m*/ *z*): 868.67 (M^+).

2^3,2^7,5^3,5^7-Tetrafluoro-2^1,2^5,2^9,5^1,5^5,5^9-hexaoctyloxy-1,1^1:4^1,1^2:4^2,1^3:4^3,1^4:4^4,1^5:4^5,1^6:4^6,1^7:4^7,1^8:4^8,1^9:4^9,1^{10}-undeciphenyl (37). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0508 g, 0.044 mmol), compound 36 (0.6018 g, 0.693 mmol), and compound 9 (0.8427 g, 1.59 mmol). The experimental procedure was as described for the preparation of compound 3 (Method 1) to give a colorless solid which was crystallized from ethyl acetate to yield a colorless powder.

Yield: 0.51 g (44%). mp: 158 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.75 (12H, m), 3.96 (12H, m), 6.94 (2H, s), 6.98 (2H, s), 7.01 (2H, s), 7.23−7.38 (10H, m), 7.53 (4H, dd), 7.59−7.70 (16H, m). MALDI-TOF MS (*m*/*z*): 1680.31 (M^+). Elemental analysis: calcd for $C_{114}H_{138}F_4O_6$: C, 81.49; H, 8.28. Found: C, 81.38; H, 8.35.

2,5-Di(2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl-4-yl)thiophene (39). Quantities were as follows: tetrakis(triphenylphosphine)palladium-(0) (0.0512 g, 0.044 mmol), compound **38** (0.4108 g, 1.70 mmol), and compound **9** (2.00 g, 3.77 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a pale yellow solid which was crystallized from ethanol-ethyl acetate (9:1) to yield a pale yellow powder.

Yield: 0.87 g (49%). mp: 60 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, m), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.69 (4H, quint), 1.72 (4H, quint), 3.95 (4H, t), 3.97 (4H, t), 7.01 (2H, s), 7.04 (2H, s), 7.29−7.47 (8H, m), 7.57−7.76 (12H, m). MALDI-TOF MS (*m*/*z*): 1053.56 (M^+). Elemental analysis: calcd for $C_{72}H_{92}O_4S$: C, 82.08; H, 8.80; S, 3.04. Found: C, 81.97; H, 8.89; S, 3.12.

5,5′-Di(2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl-4-yl)-2,2′-bithiophene (40). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0531 g, 0.046 mmol), compound **15** (0.5502 g, 1.70 mmol), and compound **9** (2.00 g, 3.77 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a yellow solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a yellow powder.

Yield: 0.69 g (36%). mp: 135 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, m), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.65 (4H, quint), 1.70 (4H, quint), 3.93 (4H, t), 3.96 (4H, t), 6.97 (2H, s), 7.02 (2H, s), 7.28−7.45 (10H, m), 7.55−7.70 (12H, m). MALDI-TOF MS (*m*/*z*): 1135.69 (M^+). Elemental analysis: calcd for $C_{76}H_{94}O_4S_2$: C, 80.38; H, 8.34; S, 5.65. Found: C, 80.32; H, 8.39; S, 5.73.

5,5″-Di(2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl-4-yl)-2,2′:5′,2″-terthiophene (41). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0507 g, 0.044 mmol), compound **16** (0.6937 g, 1.71 mmol), and compound **9** (2.00 g, 3.77 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a yellow solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a yellow powder.

Yield: 0.87 g (42%). mp: 121 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, m), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.65 (4H, quint), 1.70 (4H, quint), 3.93 (4H, t), 3.96 (4H, t), 6.98 (2H, s), 7.01 (2H, s), 7.27−7.46 (12H, m), 7.55−7.70 (12H, m). MALDI-TOF MS (*m*/*z*): 1217.81 (M^+). Elemental analysis: calcd for $C_{80}H_{96}O_4S_3$: C, 78.90; H, 7.95; S, 7.90. Found: C, 78.81; H, 8.03; S, 7.98.

5,5″-Di(2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl-4-yl)-2,2′:5′,2″:5″, 2‴-quaterthiophene (42). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (0.0514 g, 0.044 mmol), compound **18** (0.8319 g, 1.70 mmol), and compound **9** (2.00 g, 3.77 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a yellow solid which was crystallized from ethanol-ethyl acetate (1:2) to yield a yellow powder.

Yield: 1.00 g (45%); mp: 159 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (12H, m), 1.20−1.40 (32H, m), 1.48 (8H, quint), 1.65 (4H, quint), 1.70 (4H, quint), 3.93 (4H, t), 3.96 (4H, t), 6.98 (2H, s), 7.01 (2H, s), 7.27−7.48 (14H, m), 7.55−7.70 (12H, m). MALDI-TOF MS (*m*/*z*): 1299.94 (M^+). Elemental analysis: calcd for $C_{84}H_{98}O_4S_4$: C, 77.61; H, 7.60; S, 9.87. Found: C, 77.54; H, 7.63; S, 9.90.

4,4″-Di(5-bromothiophen-2-yl)-2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl (43). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.1182 g, 0.102 mmol), compound **38** (3.41

g, 0.014 mol), and compound **24** (2.00 g, 3.48 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a yellow solid which was crystallized from ethyl acetate to yield a yellow powder.

Yield: 0.60 g (21%). mp: 151 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.70 (4H, quint), 3.93 (4H, t), 7.00 (2H, s), 7.05 (2H, d, J = 3.8 Hz), 7.10 (2H, d, J = 3.8 Hz), 7.60 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 808.77 (M^+).

2′,5′-Dioctyloxy-4,4″-di[5-(2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl-4-yl)thiophen-2-yl]-1,1′:4′,1″-terphenyl (44). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0506 g, 0.044 mmol), compound **43** (0.5044 g, 0.624 mmol), and compound **9** (0.7548 g, 1.42 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a yellow solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a yellow powder.

Yield: 0.65 g (64%). mp: 72 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, m), 1.20−1.40 (48H, m), 1.48 (12H, m), 1.72 (12H, m), 3.96 (12H, m), 7.01 (2H, s), 7.03 (2H, s), 7.04 (2H, s), 7.33−7.42 (10H, m), 7.60−7.73 (20H, m). MALDI-TOF MS (*m*/*z*): 1620.40 (M^+). Elemental analysis: calcd for $C_{110}H_{138}O_6S_2$: C, 81.53; H, 8.68; S, 3.96. Found: C, 81.49; H, 8.70; S, 4.02.

5-Bromo-5″-cyano-2,2′:5′,2″-terthiophene (46). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.1521 g, 0.132 mmol), compound **15** (4.00 g, 0.012 mmol), and compound **45** (2.03 g, 0.013 mol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give a red-brown solid which was crystallized from ethanol-ethyl acetate (1:1) to yield a red-brown powder.

Yield: 1.46 g (35%). mp: 161 °C. ^{1}H NMR ($CDCl_3$): δ 6.95 (1H, d, J = 3.5 Hz), 7.00 (1H, d, J = 3.5 Hz), 7.05 (1H, d, J = 3.5 Hz), 7.12 (1H, d, J = 3.5 Hz), 7.18 (1H, d, J = 3.5 Hz), 7.52 (1H, d, J = 3.5 Hz). MS (*m*/*z*): 353 (M^+), 351 (M^+).

4,4″-Di(5″-cyano-2,2′:5′,2″-terthiophen-5-yl)-2′,5′-dioctyloxy-1,1′:4′,1′-terphenyl (47). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0568 g, 0.049 mmol), compound **46** (1.00 g, 2.84 mmol), and compound **24** (0.7503 g, 1.31 mmol). The experimental procedure was as described for the preparation of compound **3** (Method 1) to give an orange solid which was crystallized from ethyl acetate to yield an orange powder.

Yield: 0.39 g (29%). Transitions (°C): Cryst 204 N 343 Iso. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.48 (4H, quint), 1.70 (4H, quint), 3.93 (4H, t), 6.98 (2H, s), 7.03 (2H, d, J = 3.5 Hz), 7.06 (2H, d, J = 3.5 Hz), 7.10 (2H, d, J = 3.5 Hz), 7.15 (2H, d, J = 3.5 Hz), 7.20 (2H, d, J = 3.5 Hz), 7.55 (2H, d, J = 3.5 Hz), 7.60 (8H, 2xd). MALDI-TOF MS (*m*/*z*): 1029.49 (M^+). Elemental analysis: calcd for $C_{60}H_{56}N_2O_2S_6$: C, 70.00; H, 5.48; N, 2.72; S, 18.69. Found: C, 69.89; H, 5.53; N, 2.79; S, 18.76.

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