Towards a general solid phase approach for the iterative synthesis of conjugated oligomers using a germanium based linker - first solid phase synthesis of an oligo-(triarylamine)†

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The development of a germanium-based linker system for the solid phase synthesis (SPS) of 3-(*n*-hexyl)thiophene oligomers and the first SPS of triarylamine oligomers *via* iterative chain extension is described. The efficiency of the key steps in the oligomer syntheses and their compatibility with the germanium linker are demonstrated by the SPS of bi-[3-(*n*-hexyl)thiophene] **19** and ter-(triarylamine) **50**. The use of a germanium-based linker in combination with appropriately selected silicon-based blocking/protecting groups allows double coupling to drive the key cross coupling steps to completion hence minimising deletion sequences and also allows for traceless and potentially functionalisative cleavage from the resin. The latter feature has yet to be fully explored but towards this end the first *ipso*-borodegermylation reaction of a 2-germyl-3-(*n*-hexyl)thiophene is presented.

Introduction

π-Conjugated oligomers have received considerable attention recently as active materials for the construction of electronic and photonic devices such as organic light emitting diodes (OLEDs),[1] organic field-effect transistors (OFETs),[2] and photovoltaic devices (PVDs).[3] The ideal materials for such devices should display high stability and processibility during fabrication and high charge mobility and environmental stability during operation.[4] Many π-conjugated oligomeric materials have been reported in the literature which satisfy these requirements to varying degrees, including oligo-(3-alkylthiophene)s,[5] oligo-(fusedthiophene)s,[6] oligo-(dialkylfluorene)s,[7] oligo-(triarylamine)s[8–10] and alternating and block co-oligomers thereof. To obtain high charge mobilities, long-range order in the solid state and very high levels of purity are generally required.[11] We have been interested both in oligo-(3-alkylthiophene)s and oligo-(triarylamine)s as charge transport materials for potential use as p-type materials in field effect transistors (FETs) and in electroreprographic/electroluminescent devices, respectively.

Conventional solution phase chemistry has been used to synthesise monodisperse oligomeric oligo-(3-alkylthiophene)s[12–14] and oligo-(triarylamine)s[15–17] using repetitive transition metal catalysed cross-coupling. However, control over the structure of such materials is notoriously arduous due to difficulties in separating the target oligomer from residual lower molecular weight truncated oligomers and starting materials with closely similar chromatographic properties. At the outset of the work described herein, there was emerging evidence from the labs of Fréchet,[18] Tour[19] and Bäuerle[11,20–24] that Solid Phase Synthesis (SPS)[25] could constitute a useful technique for the preparation of oligo-(3-alkyl/arylthiophene)s and provide an attractive solution to some of these purification issues. However, the linker systems employed in these pioneering studies offered little flexibility for control over the end groups of the oligomers and limited prospects for generalisation to other types of oligomer. We were therefore inspired to try to develop a general SPS platform for the efficient preparation of a variety of high purity, regioregular, homo- and heteromonomer based π-conjugated oligomers. In addition, we wanted to design a system that would allow for the formation of α,ω-differentiated telechelic units for block co-oligomer preparation and for electronic property tuning as a function of the nature of the end-capping unit. We were also particularly concerned to develop protocols that would minimise the occurrence of truncated oligomers as the result of incomplete conversion during each iterative cross-coupling step.

Here, we describe development of a germanium-based linker suitable for the SPS of π-conjugated oligomers and proof of concept for its employment for the SPS of an oligo-[3-(*n*-hexyl)thiophene] and for the first SPS of an oligo-(triarylamine). The chemistry employed for both the oligo-[3-(*n*-hexyl)thiophene] and the oligo-(triarylamine) SPS was first developed on solution model systems and this work has already been published.[26,27]

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† Electronic supplementary information (ESI) available: Experimental procedures for **1b–c**, **6**, **8b–e**, **9b–e**, **10b–e**, **12–20**, **23–28**; copies of ^{1}H and ^{13}C spectra for new compounds **1b**, **1c**, **8a–e**, **9a–e**, **10a–e**, **12–18**, **20**, **23–26**, **28** and **50**, ^{1}H MAS NMR spectra for resins **30–36** and gel phase ^{13}C spectra for resins **39–41** and **43–49**, and HPLC traces for **19** and **50**. See DOI: 10.1039/b703022c

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Consequently, the following provides full details of the evolution of those solution protocols, in which a germanium-based linker having two methyl 'spectator' groups was used, into more robust SPS protocols employing a germanium-based linker having two *p*-tolyl spectator groups.[28] This change in linker was necessitated by our finding in solution that the lability of immobilised oligomers, particularly oligo-[3-(*n*-hexyl)thiophene]s, towards unwanted cleavage from the linker by adventitious acid increased as the oligomers grew and our desire to develop a robust platform for SPS of many varied oligomers with wide scope.

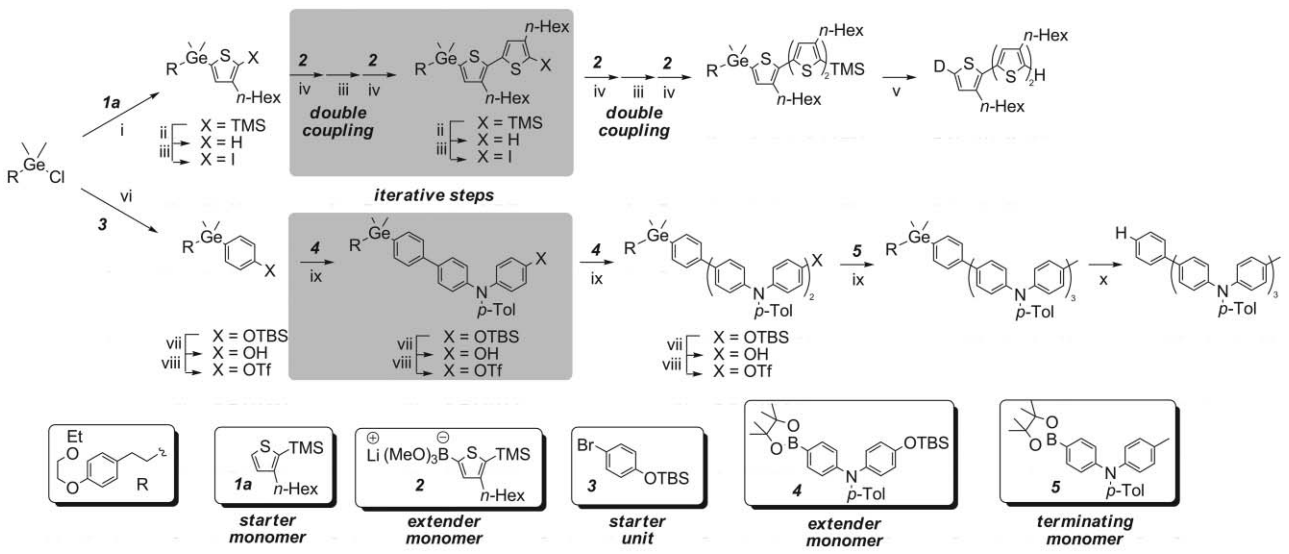
Results and discussion

Our choice of a germanium-based linker system[29–31] as the foundation on which to build our SPS approach to π-conjugated oligomers was primarily influenced by the need to employ a linker that would be robust to a wide range of aromatic/heteroaromatic metalation conditions [*e.g.* halogen–metal exchange, directed *ortho* metalation (D*o*M)][32] and to transition metal catalysed cross-coupling conditions (*e.g.* Suzuki coupling, Buchwald–Hartwig amination)[33,34] and which would allow traceless[35] and functionalisative[36] cleavage from the solid support. Germanium-based linkers were considered to be excellent candidates for this role as the key arylgermane bond connecting the solid support to the growing oligomer terminus was expected to display excellent stability towards strongly basic conditions whilst being susceptible to cleavage (*via ipso*-substitution) by a wide range of electrophiles. These expectations followed particularly from our previous work in which a germanium-based linker was shown to exhibit enhanced stability towards basic/nucleophilic conditions as compared to silicon-based counterparts[26] and model studies in which cleavage of the same linker by TFA, NCS, Br_2, ICl[30] and RCOCl/$AlCl_3$[37] could be effected with concomitant introduction of H, Cl, Br, I and COR functions at the position of former attachment to the linker. However, as noted above, during the early development of the oligomer chemistry in solution it became apparent that susceptibility to cleavage by electrophiles was a property of the linker that would require careful tuning to allow, on the one hand, facile functionalisative cleavage from the solid support at the end of the synthesis and, on the other hand, adequate stability during the iterative oligomer extension steps.[38]

The iterative oligomer assembly processes that we developed for the preparation of oligo-[3-(*n*-hexyl)thiophene]s and oligo-(triarylamine)s in solution are summarised below (Scheme 1).

For the preparation of the ter-[3-(*n*-hexyl)thiophene] in solution, the synthesis involved coupling of lithiated trimethylsilyl (TMS) blocked 3-(*n*-hexyl)thiophene 'starter monomer' **1a** to a dimethylgermylchloride linker model,[39] chemoselective removal of the TMS blocking group, activation of the 'oligomer' terminus as an iodide, and then Suzuki double coupling with a TMS-blocked 3-(*n*-hexyl)thiophene boronate salt 'extender monomer' **2**. The sequence was then repeated on the resulting dimer, starting with removal of the TMS blocking group. The resulting trimer was then cleaved from the linker tracelessly using acid. The process relies critically on the orthogonal susceptibility of the TMS and aryldimethylgermyl groups towards *ipso*-protodegermylation by fluoride ions: the TMS group is selectively removed by CsF in DMF at 60 °C without affecting the linker. Additionally, the double coupling process that is employed to drive the coupling steps to completion (and so minimise formation of truncated oligomers) relies on the stability of both these groups during the activation and the Suzuki coupling steps.[26] It was envisaged that, in principle, once optimised for SPS, the iterative steps for monomer introduction and activation could be repeated to provide an oligomer of any desired length.

For the preparation of the ter-(triarylamine) in solution, a similar sequence of steps was developed involving coupling of lithiated *tert*-butyldimethylsilyl (TBS) ether blocked phenol 'starter unit' **3**



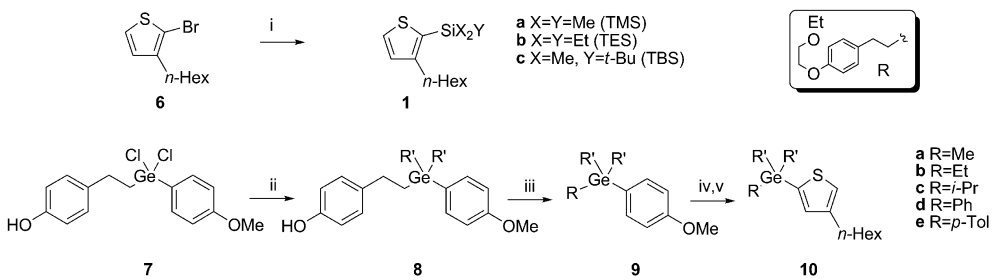
Scheme 1 The preparation of a ter-[3-(*n*-hexyl)thiophene][26] and a ter-(triarylamine)[27] in solution by iterative coupling processes. *Reagents and conditions*: i) **1a**, LDA, THF, −50 °C; ii) CsF, DMF, 60 °C; iii) *n*-BuLi, THF, −50 °C then ICH_2CH_2I, dark; iv) **2**, $Pd(PPh_3)_4$, DMF, 60 °C; v) DCl, $CDCl_3$; vi) **3**, *n*-BuLi, THF, −78 °C then toluene, RT; vii) TBAF, THF, RT; viii) Tf_2O, pyridine, 0 °C; ix) **4** (or **5**), $Pd(PPh_3)_4$, Na_2CO_3, DME, 80 °C; x) 1% TFA in CH_2Cl_2, RT.

to the same dimethylgermylchloride linker model, chemoselective removal of the TBS-ether blocking group, activation of the resulting phenol as a triflate ester, and then Suzuki coupling with a TBS ether blocked triarylamine boronic ester extender monomer **4**. The sequence was then repeated on the resulting monomer, starting with removal of the TBS ether. The resulting dimer was then TBS deprotected, activated and capped-off by Suzuki coupling to triarylamine boronic ester 'terminating monomer' **5** to give the trimer which was then cleaved from the linker tracelessly using acid. This process relies critically on the orthogonal susceptibility of the TBS ether and aryldimethylgermyl groups towards cleavage by fluoride ions: the TBS ether is selectively removed by tetra-*n*-butylammonium fluoride (TBAF) in THF at RT without affecting the linker. For this 'proof-of-principle' synthesis, double coupling was not performed; however, the system was designed to allow for this *via* reactivation of the crude coupled product with trifluoromethanesulfonic anhydride and then re-coupling to drive any phenol-terminated oligomer (from hydrolysis of the triflate during coupling) through to the homologated product. Again, it was envisaged that, in principle, once optimised for SPS, the iterative steps for monomer introduction and activation could be repeated to provide an oligomer of any desired length.

However, despite the complete orthogonality of the linker to the fluoride blocking group deprotection steps in these studies, the TMS blocking group employed in the oligo-[3-(*n*-hexyl)thiophene] sequence proved to be susceptible to partial cleavage by traces of adventitious acid once the oligomer reached the tetramer length (*e.g.* during NMR spectroscopy in $CDCl_3$). This finding forced us to develop a new thiophene silyl blocking group/germanium linker combination which retained the orthogonal stability of the silyl *vs.* germyl linkages towards fluoride ions but for which both partners displayed enhanced stability towards acid.

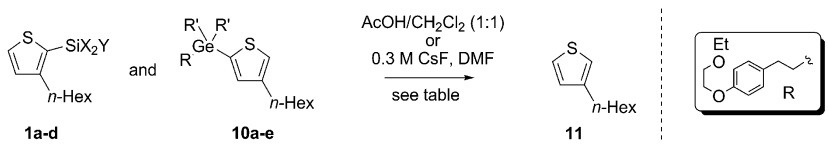
Consequently, three silyl protected 3-(*n*-hexyl)thiophenes (TMS, TES and TBS thiophenes **1a–c**) and five germanium-based linkers containing different spectator groups (dimethyl, diethyl, di-*iso*-propyl, diphenyl and di-*p*-tolylgermylthiophenes **10a–e**) were prepared (Scheme 2). Noteworthy during the execution of this chemistry was the high degree of selectivity achievable for protonolysis of the *p*-anisole group over either phenyl or *p*-tolyl groups when employing HCl in Et_2O at RT (*i.e.* step iv).

These silyl and germyl thiophenes were evaluated for their stability towards both acid ($AcOH–CH_2Cl_2$, 1 : 100) and fluoride (~0.3 M CsF in DMF). Screening consisted of monitoring by ^1H NMR while the temperature was stepped up from 25 to 60 to 110 °C over 72 h (Table 1).



Scheme 2 Preparation of silyl blocked 3-(*n*-hexyl)thiophenes **1a–d** and linker candidates **10a–e**. *Reagents and conditions*: i) *n*-BuLi, THF, −78 °C then YX_2SiCl → RT; ii) R′MgBr/Cl, toluene, 110 °C; iii) $EtOCH_2CH_2Cl$, *n*-Bu_4NI, Cs_2CO_3, MeCN, 85 °C; iv) 1 M HCl, Et_2O, RT; v) 5-lithio-3-(*n*-hexyl)thiophene [from 3-(*n*-hexyl)thiophene and LDA], THF, −50 °C → RT.

Table 1 Acid and fluoride induced *ipso*-desilylation/degermylation of silylthiophenes **1a–c** and germylthiophenes **10a–e**



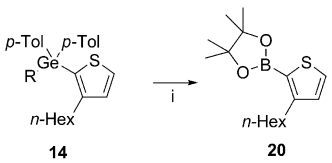
	Cleavage conditions[a]					
	AcOH			CsF		
Substrate	25 °C	60 °C	110 °C	25 °C	60 °C	110 °C
1a (X = Y = Me, TMS)	✗	—	—	✗	—	—
1b (X = Y = Et, TES)	~	✗	—	✗	—	—
1c (X = Me, Y = *t*-Bu, TBS)	✓	✓	✓	✗	—	—
10a (R′ = Me)	~	✗	—	✓	✓	✓
10b (R′ = Et)	~	✗	—	✓	✓	✓
10c (R′ = *i*-Pr)	~	✗	—	✓	✓	✓
10d (R′ = Ph)	✓	✓	✓	✓	✓	✓
10e (R′ = *p*-Tol)	✓	✓	✓	✓	✓	✓

[a] Key: ✓ = stable; ~ = partial cleavage; ✗ = complete cleavage; — = N/A.

As a result of this stability screening process, the TBS group was selected as the most suitable silyl blocking group for SPS since TBS thiophene **1c** was the most acid stable. As this group also showed noticeably greater stability towards fluoride than the TMS group it was decided to use it in combination with the linker having *p*-tolyl spectator groups as the thiophene bound *via* this linker (**10e**) was markedly more stable towards acid than the dialkyl linkers and because the *p*-tolyl methyl groups were anticipated to provide a convenient marker for NMR reaction monitoring (*cf.* the diphenyl analogue **10d**, which was equally acid stable). Using this blocking group/germyl spectator group combination the key iterative steps of the envisioned oligo-[3-(*n*-hexyl)thiophene] SPS were re-investigated in solution (Scheme 3).

For this work, the position of the *n*-hexyl side chain of the thiophene unit was reversed relative to that of the previous solution phase work (*i.e.* Scheme 1, above). This change was made mainly because 2-TBS-4-(*n*-hexyl)thiophene **12** could be obtained on a preparative scale with very high purity more easily than 2-TBS-3-(*n*-hexyl)thiophene **1c**.[40] Additionally, we had shown previously that the position of the *n*-hexyl chain had little effect on the susceptibility of the linker towards cleavage,[26] and with the now more robust linker it was anticipated that these differences would be insignificant. Thus, 2-TBS-4-(*n*-hexyl)thiophene **12** was readily immobilised onto di-*p*-tolyl linker model by lithiation with LDA then quenching with the germyl chloride derived from *p*-anisylgermane **10e** (73%) to give TBS protected compound **13**. TBS deprotection was achieved using CsF in DMF at 110 °C (*cf.* 60 °C previously) for 24 h to give germylthiophene **14** in 95% yield and activation was achieved as in solution using LDA/1,2-diiodoethane to give the iodide **15** (90%). In the previous solution phase work it had been necessary to employ boronate salt **2** as the monomer such that Suzuki coupling could be achieved under base-free conditions to avoid desilylation; with the new blocking group/linker combination this was no longer necessary and coupling to give bithiophene **17** (60%) could be achieved without any traces of desilylation using pinacolato boronic ester **16** under fairly standard conditions employing K_3PO_4 as base. No attempt was made to optimise this coupling at this stage as it was decided that this would be best performed 'on-resin'. Cleavage of the TBS group from bithiophene was readily achieved once again using CsF in DMF at 110 °C (→**18**, 99%) and cleavage of the linker was readily achieved using TFA in CH_2Cl_2 at RT to give bithiophene **19** in 97% yield.

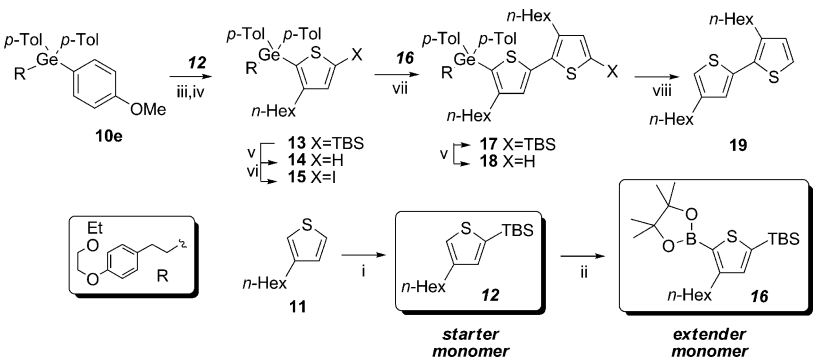
Linker cleavage with concomitant introduction of a pinacolato boronic ester at the previous point of attachment was also briefly explored using germylthiophene **14** as a substrate. As indicated above, it was envisaged that this type of functionalisative cleavage would provide expeditious access to α, ω-differentiated telechelic oligo-(thiophene)s for block co-oligomer preparation. Although *ipso*-borodesilylation has been reported previously,[41–49] to the best of our knowledge *ipso*-borodegermylation has not. We were able to effect the desired transformation on germylthiophene **14** to give pinacolato boronic ester **20** in an unoptimised 30% yield using BCl_3 in CH_2Cl_2–propylene oxide at −78 °C followed by addition of pinacol. The mass balance was protodegermylated material [*i.e.* 3-(*n*-hexyl)thiophene (**11**)]; no starting material remained (Scheme 4).



14 **20**

Scheme 4 *ipso*-Borodegermylation of germylthiophene **14** to give boronic ester **20** in solution. *Reagents and conditions*: i) propylene oxide, CH_2Cl_2, BCl_3, −78 °C, then pinacol, RT.

We were now in a position to transfer the chemistry to the solid phase. Two resins were selected for these studies: Merrifield and Quadragel®. The former, has the advantage of low cost and good handling properties but displays limited swelling in *e.g.* THF. The latter, which is a TEG [tetra(ethyleneglycol)] grafted *p*-hydroxy-PS resin, is more expensive and has a tendency to stick to glassware, but has excellent swelling in *e.g.* THF. In the event, initial studies using Merrifield demonstrated that although the di-*p*-tolyl linker **8e** could be readily introduced onto the resin using *n*-Bu_4NI, Cs_2CO_3, MeCN at 85 °C (*i.e.* Williamson etherification), and could be activated as the germyl chloride using excess HCl in Et_2O–CH_2Cl_2, the subsequent reaction with the lithiated TBS protected 4-(*n*-hexyl)thiophene **12** in THF at −40 °C proceeded with only ∼25% conversion as judged by



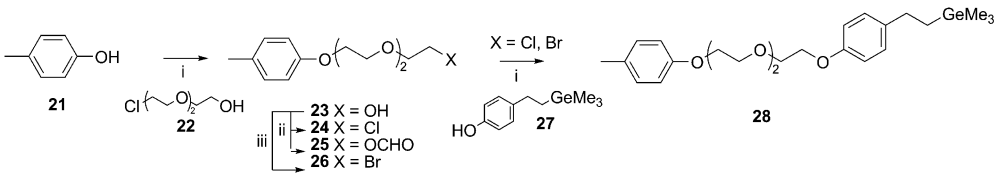
Scheme 3 Solution studies on the iterative steps for oligo-[3-(*n*-hexyl)thiophene] synthesis using the TBS thiophene/di-*p*-tolylgermyl linker combination. *Reagents and conditions*: i) LDA, THF, TBSCl, −50 °C → RT; ii) LDA, THF, 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane, −50 °C → RT; iii) 1 M HCl, Et_2O, RT; iv) 5-lithio-2-TBS-4-(*n*-hexyl)thiophene (from **12** and LDA), THF, −50 °C → RT; v) CsF, DMF, 110 °C; vi) LDA, THF, −40 °C then ICH_2CH_2I, dark; vii) **16**, K_3PO_4, $Pd(PPh_3)_4$, DMF, 60 °C; vi) 33% TFA in CH_2Cl_2, RT.

^{1}H MAS NMR (integrating the TBS methyl groups against the linker *p*-tolyl methyl groups). This was not entirely unexpected due to the aforementioned limited swelling of the resin in THF, particularly at the low temperature required for this reaction. Consequently, our attention turned to Quadragel®. As this resin is supplied hydroxyl terminated and our preference was to employ the above Williamson etherification conditions for the immobilisation step rather than Mitsunobu conditions[31] on cost grounds, the first step was to effect halogenation of the resin. Initial trials at chlorination using $SOCl_2$ in CCl_4 with catalytic DMF[50] led to the appearance of an unexplained peak in the IR spectrum of the product resin at 1725 cm^{-1} so we decided to use triethyleneglycol etherified *p*-cresol **23** as a model compound on which to optimise the procedure (Scheme 5).

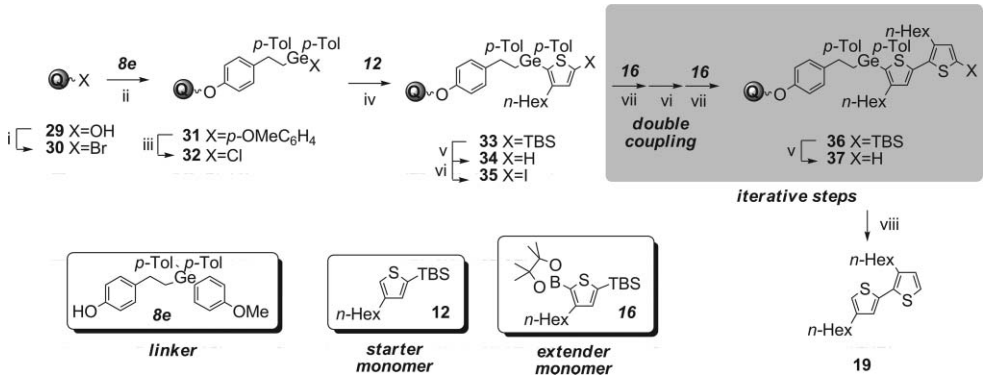
The model compound **23** was readily prepared by the alkylation of a two-fold excess of *p*-cresol (**21**) with chloride **22** (as the product **23** and the chloride **22** were essentially inseparable by chromatography). Chlorination using $SOCl_2$ in CCl_4 with catalytic DMF yielded the desired chloride **24** (89%) and formate ester **25** (9%). The formate ester had a strong carbonyl stretching absorption in the IR at 1725 cm^{-1} thereby explaining the result observed on resin. As omitting the DMF resulted in an unacceptably sluggish reaction, bromination using PPh_3–CBr_4 in CH_2Cl_2 was investigated. This procedure resulted in very clean conversion to the corresponding bromide **26** in 97% yield. The isolated chloride **24** and bromide **26** were then subjected in parallel to etherification with trimethylgermyl linker **27**.[50] As both reactions gave comparable yields of the immobilised linker **28** (87% and 84%, respectively) it was decided to employ the bromination procedure for the SPS work. The SPS of bi-[3-(*n*-hexyl)thiophene] **19** using iterative chain extension with double coupling is outlined below (Scheme 6).

Bromination of Quadragel® (**29**, 0.93 mmol g^{-1} → **30**, 0.88 mmol g^{-1}) proceeded smoothly as did the immobilisation of the di-(*p*-tolyl)*p*-anisyl linker **8e** by Williamson etherification. The resulting resin **31** (0.52 mmol g^{-1}) was activated with HCl in ether (→**32**, 0.54 mmol g^{-1}) and the starter monomer, TBS-blocked 4-(*n*-hexyl)thiophene **12**, was then efficiently introduced as its lithiated derivative. Removal of the TBS blocking group from the resulting resin bound thiophene proceeded selectively using CsF in DMF at 110 °C (**33**, 0.40 mmol g^{-1} → **34**, 0.42 mmol g^{-1}) without detectable cleavage of the arylgermane. Sequential iodination (→**35**, 0.40 mmol g^{-1}) and Suzuki cross-coupling with TBS-blocked thiophene boronic ester extender monomer **16** also proceeded smoothly to give the resin bound bithiophene **36** with high efficiency. It was found that no optimisation of this step was required relative to the solution phase conditions (Scheme 3). Indeed the cross-coupling was so efficient that the double-coupling sequence was almost unnecessary for enhancing the efficiency of coupling: after double coupling a final loading level of 0.35 mmol g^{-1} was achieved and HPLC analysis of TFA cleaved crude samples of bithiophene **19** before and after double coupling had purities of 94% and 96%, respectively. Bithiophene **19** was fully characterised by ^{1}H NMR, ^{13}C NMR, IR, and HRMS. All the steps in the sequence were monitored by ^{1}H MAS NMR and appeared to proceed to ~100% conversion (see Fig. 1, Electronic Supplementary Information†). Loading levels were determined by elemental analysis and/or NMR integration and/or recovery of reagents (see experimental). The overall 'yield' for the double-coupled material from Quadragel® bromide (**30**) over the nine steps was ~28%.

For the oligo-(triarylamine) SPS, the same di-*p*-tolylgermyl linker was employed but using HypoGel® in place of Quadragel® as the solid support. HypoGel® generally has similar properties



Scheme 5 Optimisation of the resin halodehydration/linker attachment steps using soluble model system **23**. *Reagents and conditions*: i) *n*-Bu_4NI, Cs_2CO_3, MeCN, 85 °C; ii) $SOCl_2$, DMF, CH_2Cl_2, RT; iii) PPh_3, CBr_4, CH_2Cl_2, RT.



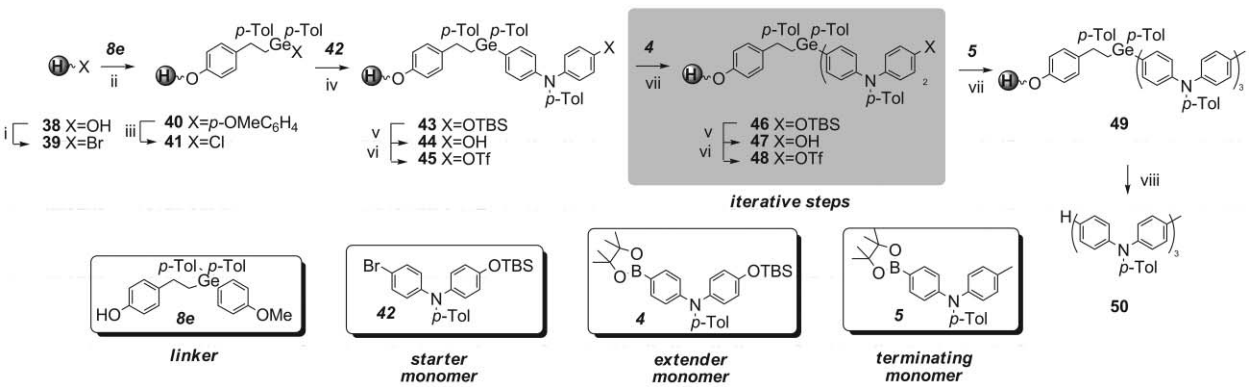
Scheme 6 The preparation of bi-[3-(*n*-hexyl)thiophene] **19** by SPS on Quadragel®. *Reagents and conditions*: i) PPh_3, CBr_4, CH_2Cl_2, RT; ii) **8e**. *n*-Bu_4NI, Cs_2CO_3, MeCN, 85 °C; iii) 1 M HCl, Et_2O, RT; iv) 5-lithio-2-TBS-4-(*n*-hexyl)thiophene (from **12** and LDA), THF, −40 °C → RT; v) CsF, DMF, 110 °C; vi) LDA, THF, −40 °C then ICH_2CH_2I, dark; vii) **16**, K_3PO_4, $Pd(PPh_3)_4$, DMF, 60 °C; viii) 33% TFA in CH_2Cl_2, RT.

to Quadragel® but differs in that it a polydisperse PEG grafted *p*-hydroxyethyl-PS resin having on average five oxyethyl repeat units (*cf.* monodisperse TEG grafted *p*-hydroxy-PS). HypoGel® was preferred for this work because in our hands it provided superior gel-phase ^{13}C NMR spectra relative to Quadragel®, allowing the synthesis to be monitored without the need for regular access to an NMR spectrometer with an MAS probe. For the envisaged SPS it was not considered necessary to change the TBS ether phenol blocking group employed in the solution phase studies as this had proved amply robust and was anticipated to retain its ability to be orthogonally removed by TBAF when paired with the new linker. However, for the SPS it was decided to initiate the synthesis by introduction of bromotriarylamine starter monomer **42** rather than the 4-bromophenol derivative **3** used in the solution studies. This modification allows the oligomer synthesis to proceed by immediate monomer introduction and requires no additional 'off-resin' monomer synthesis as the starter monomer **42** is an intermediate in the synthesis of extender monomer **4**.[27] The SPS of ter-(triarylamine) **50** using iterative chain extension is outlined below (Scheme 7).

Bromination of HypoGel® (**38**, 0.80 mmol g^{-1} → **39**, 0.80 mmol g^{-1}) and subsequent immobilisation of the di-(*p*-tolyl)*p*-anisyl linker **8e** by Williamson etherification (→**40**, 0.48 mmol g^{-1}) proceeded smoothly as on the Quadragel®. Activation with HCl in ether was also uneventful, providing the germyl chloride resin **41** cleanly (0.49 mmol g^{-1}). Immobilisation of the starter monomer using lithiated triarylamine bromide **42** afforded triarylamine TBS ether resin **43** (0.37 mmol g^{-1}). Selective cleavage of the TBS ether group was achieved using TBAF to give phenol resin **44** (0.38 mmol g^{-1}) with no detectable cleavage of the arylgermane linkage. Conversion of the phenol function to the triflate derivative using trifluoromethanesulfonic anhydride was carried out in anhydrous pyridine to give resin **45** (0.37 mmol g^{-1}) and set the stage for the Suzuki cross-coupling step. Triarylamine boronic ester extender monomer **4** was cross-coupled to aryl triflate resin **45** to give the triarylamine dimer resin **46** (0.34 mmol g^{-1}) using the same conditions developed for the preliminary solution studies (Scheme 1).[27] An excess of extender monomer **4** was used to drive the reaction to completion. Deprotection of the TBS ether and subsequent conversion to triflate was repeated to give resins **47** (0.33 mmol g^{-1}) and **48** (0.30 mmol g^{-1}), respectively. Finally, triarylamine boronic ester terminating monomer **5** was cross-coupled to triflate resin **48** to yield resin **49** (0.30 mmol g^{-1}). Release of oligomer from the resin **49** was achieved by electrophilic *ipso*-protodegermylation using a 1% solution of trifluoroacetic acid (TFA) in CH_2Cl_2. Purification by FC yielded the target H-capped ter-(triarylamine) **50** which was characterised by ^1H NMR, ^{13}C NMR and HRMS. Its purity was >97% by HPLC. All the steps were conveniently monitored by ^{13}C gel-phase NMR (see Figs 2 and 3, Electronic Supplementary Information†) and loading levels were determined by elemental analysis (see experimental). The overall 'yield' from HypoGel® bromide (**40**) over the 10 steps was ~28%.

Conclusions

In summary, we have described the development of a germanium-based linker system for the SPS of 3-(*n*-hexyl)thiophene oligomers and for the first SPS of triarylamine oligomers *via* iterative chain extension protocols. The germanium-based linker provides a robust platform for the chain extension steps, allows orthogonal removal of temporary TBS thiophene and TBS phenolic ether blocking groups following each iteration using fluoride, and allows for traceless or functionalisative cleavage from the resin. The efficiency of the key steps in the oligomer syntheses and their compatibility with the germanium linker have been demonstrated. The key iterative steps in both processes are: i) cross coupling of a terminally blocked extender monomer to a linker bound activated oligomer terminus, ii) selective deprotection of the now terminal blocking group, iii) activation of the resulting functionality to one suitable for cross coupling and then repetition of the cycle for the desired number of iterations. The use of a blocking group in this fashion allows double coupling to drive each cross coupling step to completion and hence minimise deletion sequences; this tactic has been validated for the oligo-(thiophene) series. The first *ipso*-borodegermylation reaction has also been performed in a model study for the potential cleavage of a germanium bound oligo-[3-(*n*-hexyl)thiophene] from the resin with concomitant functionalisation of the oligomer as a terminal boronic ester; a process of potential utility for block co-oligomer synthesis. We are currently adapting these synthetic strategies to accommodate other monomers and expanding the scope of the functionalisative



Scheme 7 The preparation of ter-(triarylamine) **50** by SPS on HypoGel®. *Reagents and conditions*: i) PPh_3, CBr_4, CH_2Cl_2, RT; ii) *n*-Bu_4NI, Cs_2CO_3, MeCN, 85 °C; iii) 1 M HCl in Et_2O, RT; iv) *n*-BuLi, THF, −78 °C; v) TBAF, THF, RT; vi) Tf_2O, pyridine, 0 °C; vii) $Pd(PPh_3)_4$, Na_2CO_3, DME, 80 °C; vii) 1% TFA in CH_2Cl_2, RT.

cleavage protocols to provide new oligomers of potential utility as novel electroactive materials.

Experimental

General directions

All reactions were performed under anhydrous conditions and an inert atmosphere of N_2 in the oven or flame dried glassware. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials, unless otherwise indicated. Reagents were used as obtained from commercial sources or purified according to known procedures.[51] Quadragel® resin was purchased from Avecia Ltd. [nominal loading level (LL) 930 μmol g^{-1}] and is a DVB crosslinked *p*-hydroxy-PS-based resin etherified with a monodisperse TEG [tetra(ethyleneglycol)] graft terminating with a OH group. HypoGel® resin was purchased from Fluka Ltd. (nominal LL 800 μmol g^{-1}) and is a DVB crosslinked *p*-hydroxyethyl-PS-based resin etherified with a polydisperse PEG graft containing on average five oxyethyl repeat units terminating with a hydroxyl group. Flash chromatography (FC) was carried out using Merck Kiesegel 60 F_{254} (230–400 mesh) silica gel. Only distilled solvents were used as eluents. Thin layer chromatography (TLC) was performed on Merck DC-Alufolien or glass plates pre-coated with silica gel 60 F_{254} which were visualised either by quenching of ultraviolet fluorescence (λ_{max} = 254 nm) or by charring with 5% w/v phosphomolybdic acid in 95% EtOH, 10% w/v ammonium molybdate in 1 M H_2SO_4, or 10% $KMnO_4$ in 1 M H_2SO_4. Observed retention factors (R_f) are quoted to the nearest 0.05. All reaction solvents were distilled before use and stored over activated 4 Å molecular sieves, unless otherwise indicated. Anhydrous CH_2Cl_2 was obtained by refluxing over CaH_2. Anhydrous THF and Et_2O were obtained by distillation, immediately before use, from sodium/benzophenone ketyl under an inert atmosphere of N_2. Anhydrous DMF was obtained by distillation from CaH_2 under reduced pressure. Ethylene glycol was distilled immediately prior to use. Petrol refers to the fraction of light petroleum boiling between 40–60 °C. NMR *J* values are given in Hz. High Resolution Mass Spectrometry (HRMS) measurements are valid to ±5 ppm. Microanalyses were performed using a LECO CHNS 932 Analyser (N), an Atomscan 16 ICP-OES (Ge), an Orion Ion Analyser (F), and a Metrohm 716 DMS (Cl, Br). Results are quoted to the nearest ±0.1%, and are valid to 0.5% (N, Cl, Br, F) and 1.5% (Ge) of theory.

General procedure A

Lithiation of bromide **6** and subsequent reaction with a chlorosilane.

[3-(*n*-Hexyl)thiophen-2-yl]trimethylsilane 1a[52]. A solution of *n*-BuLi (787 μL, 2.2 M, 1.57 mmol) in hexanes was added dropwise to a degassed solution of bromide **6** (387 mg, 1.57 mmol) in THF (3 mL) at −78 °C. The reaction mixture was stirred for 40 min at this temperature, and then trimethylchlorosilane (600 μL, 4.73 mmol) added dropwise at −78 °C. The resulting mixture was stirred for 1 h at this temperature, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3 × 100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (pentane) to give silylthiophene **1a** as a colourless oil (329 mg, 87%). R_f 0.85 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 9H), 0.58 (t, J = 6.5, 3H), 0.95–1.10 (6H), 1.27 (m, 2H), 2.36 (t, J = 8, 2H), 6.73 (d, J = 4.5, 1H), 7.14 (d, J = 4.5, 1H); MS (CI+) m/z 240 (M^+); HRMS (CI+) calcd. for $C_{13}H_{24}SSi$ (M^+) 240.1368, found 240.1361.

General procedure B

reaction of germyldichloride **7** with a Grignard reagent.

4-{2-[(4-Methoxyphenyl)dimethylgermanyl]ethyl}phenol 8a. A solution of MeMgBr (40.0 mL, 3.0 M, 1.20 mmol) in Et_2O was added to a solution of *4-{[2-dichloro-(4-methoxyphenyl)germanyl]ethyl}phenol* (**7**)[38] (9.00 g, 24.2 mmol) in toluene (50 mL). The mixture was then refluxed at 110 °C for 16 h before partitioning between sat. NH_4Cl (aq) (250 mL) and Et_2O (200 mL). After extracting further with Et_2O (2 × 200 mL) the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by FC (petrol–EtOAc, 3 : 1) to give dimethylgermane **8a** as a pale yellow oil (7.55 g, 84%). R_f 0.40 (petrol–EtOAc, 3 : 1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.25 (s, 6H); 1.14 (m, 2H), 2.54 (m, 2H), 3.73 (s, 3H), 4.67 (broad s, 1H), 6.64 (d, J = 8.5, 2H), 6.84 (d, J = 9, 2H), 6.95 (d, J = 8.5, 2H), 7.29 (d, J = 9, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ −3.6 (q, 2C), 18.2 (t), 30.2 (t), 55.1 (q), 113.8 (d, 2C), 115.1 (d, 2C), 128.9 (d, 2C), 132.2 (s), 134.5 (d, 2C), 137.0 (s), 153.5 (s), 159.9 (s); IR (neat) 3401 (broad, O–H), 3020–2835 (C–H), 1612, 1592, 1569, 1513, 1500, 1462, 1443, 1358, 1279, 1246 cm^{-1}; MS (EI+) m/z 332 (M^+); HRMS calcd. for $C_{17}H_{22}Ge^{74}O_2$ (M^+) 332.0832, found 332.0824; Anal. calcd. for $C_{17}H_{22}GeO_2$: C 61.7, H 6.7, found C 62.0, H 6.6%.

General procedure C

Williamson etherification with 2-chloroethyl ethyl ether.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-methoxyphenyl)dimethylgermane 9a. To a solution of phenol **8a** (96.1 mg, 290 μmol) in acetonitrile (65 mL) was added 2-chlorodiethyl ether (70.0 μL, 638 μmol), TBAI (10.7 mg, 29.0 μmol) and caesium carbonate (153 mg, 434 μmol). The mixture was refluxed at 85 °C for 17 h then cooled and filtered. The solvent was removed *in vacuo* and the residue purified by FC (petrol–EtOAc, 20 : 1) to give ether **9a** as a pale yellow oil (105 mg, 90%). R_f 0.30 (petrol–EtOAc, 9 : 1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.25 (s, 6H), 1.16 (m, 5H), 2.54 (m, 2H), 3.52 (q, J = 7, 2H), 3.70 (t, J = 4.5, 2H), 3.73 (s, 3H), 4.01 (t, J = 4.5, 2H), 6.64 (d, J = 8.5, 2H), 6.84 (d, J = 8.5, 2H), 6.95 (d, J = 9, 2H), 7.29 (d, J = 9, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ −3.5 (q, 2C), 15.2 (q), 18.2 (t), 30.2 (t), 55.1 (q), 66.9 (t), 67.5 (t), 69.1 (t), 113.8 (d, 2C), 114.6 (d, 2C), 128.7 (d, 2C), 132.0 (s), 134.5 (d, 2C), 137.1 (s), 156.9 (s), 159.9 (s); IR (neat) 2930–2870 (C–H), 1611, 1593, 1568, 1511, 1500, 1458, 1280, 1247 cm^{-1}; MS (EI+) m/z 404 (M^+); HRMS calcd. for $C_{21}H_{30}Ge^{74}O_3$ (M^+) 404.1407, found 404.1393.

{2-[4-(2-Ethoxyethoxy)phenyl]ethyl}-(4-hexylthiophen-2-yl)dimethylgermane 10a. To germyl-*p*-anisole **9a** (1.16 g, 2.01 mmol) was added HCl in Et_2O (40.2 mL, 1.0 M, 40.2 mmol) and the reaction mixture left to stir for 16 h. The solvent was then removed *in vacuo* to give the crude germyl chloride as a brown oil [^{1}H NMR

(250 MHz, $CDCl_3$): δ 0.59 (s, 6H), 1.20–1.27 (m, 3H), 1.45–1.55 (m, 2H), 2.80 (t, J = 8, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5, 2H), 4.10 (t, J = 5, 2H), 6.85 (d, J = 8.5, 2H), 7.10 (d, J = 8.5, 2H); MS (EI+) m/z 332 (M^+); HRMS (EI+) calcd. for $C_{14}H_{23}ClGe^{74}O_2$ (M^+) 332.0598, found 332.0586]. In a separate flask, a solution of LDA (3.99 mL, 2.0 M, 7.98 mmol) in hexanes–THF–ethylbenzene (6 : 5 : 3) was added dropwise to a degassed solution of 3-(*n*-hexyl)thiophene (1.34 g, 7.98 mmol) in THF (5 mL) at −50 °C. This solution was stirred for 40 min at −40 °C, and then transferred by cannula to a degassed solution of the crude germyl chloride in THF (5 mL) at −50 °C. The resulting mixture was stirred for 1 h at −40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (100 mL), the mixture was extracted with Et_2O (3 × 100 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by FC (petrol–EtOAc, 9 : 1) to give dimethylgermylthiophene **10a** as a brown/yellow oil (741 mg, 60%). R_f 0.40 (petrol–EtOAc, 9 : 1); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.38 (s, 6H), 0.88 (t, J = 7, 3H), 1.23 (t, J = 7, 3H), 1.25–1.30 (8H), 1.58 (m, 2H), 2.62 (t, J = 8, 2H), 2.67 (t, J = 8.5, 2H), 3.59 (q, J = 7, 2H), 3.77 (t, J = 5.5, 2H), 4.09 (t, J = 5.5, 2H), 6.83 (d, J = 8, 2H), 6.96 (s, 1H), 7.06 (s, 1H), 7.11 (d, J = 8, 2H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ −2.3 (q, 2C), 14.1 (q), 15.2 (q), 19.1 (t), 22.6 (t), 29.2 (t), 30.1 (t, 2C), 30.7 (t), 31.7 (t), 66.8 (t), 67.5 (t), 69.1 (t), 114.6 (d, 2C), 124.5 (d), 128.7 (d, 2C), 134.5 (d), 136.8 (s), 139.6 (s), 144.5 (s), 157.00 (s); IR (neat) 2930–2855 (C–H), 1611, 1511, 1246 cm^{-1}; MS (EI+) m/z 464 (M^+); HRMS (EI+) calcd. for $C_{24}H_{38}Ge^{74}O_2S$ (M^+) 464.1804, found 464.1798.

Typical procedure A

Assessment of AcOH stability of a germyl/silyl thiophene.

(Table 1, entry 3). To silylthiophene **1c** (10.5 mg, 37 μmol) was added CH_2Cl_2 (500 μL) and then AcOH (5 μL). The mixture was stirred at 25 °C for 24 h, then at 60 °C for 24 h and then at 110 °C for a further 24 h, analysing by ^{1}H NMR ($CDCl_3$) for extent of conversion to 3-(*n*-hexyl)thiophene **11**.[53]

Typical procedure B

Assessment of CsF stability of a germyl/silyl thiophene.

(Table 1, entry 3). To silylthiophene **1c** (7.6 mg, 27 μmol) was added DMF (500 μL) and CsF (20 mg, 0.13 mmol). The mixture was stirred at 25 °C for 24 h, then at 60 °C for 24 h and then at 110 °C for a further 24 h, analysing by ^{1}H NMR ($CDCl_3$) for extent of conversion to 3-(*n*-hexyl)thiophene **11**.[53]

Quadragel®-Br 30. To a suspension of Quadragel® (**29**, 38.7 g, LL = 930 μmol g^{-1}, 36.0 mmol) in CH_2Cl_2 (220 mL) at 0 °C was added triphenylphosphine (10.3 g, 39.3 mmol) and carbon tetrabromide (26.0 g, 78.4 mmol). The orange reaction mixture was warmed to RT and left to stir for 24 h. The solvent was removed by filtration and the resin washed sequentially with CH_2Cl_2 (3 × 300 mL), DMF (300 mL), THF–H_2O (1 : 1, 2 × 300 mL), THF (2 × 300 mL, and MeOH (2 × 300 mL). The resin was then dried *in vacuo* to give resin **30** as yellow grains (37.5 g, LL = 880 μmolg^{-1}. ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 1.00–1.75 [C*H*(Ar)C*H*$_2$], 1.75–2.20 [C*H*(Ar)C*H*$_2$], 3.50–3.60 (OC*H*$_2$), 3.75–4.20 (OC*H*$_2$), 6.30–6.85 (Ar*H*), 6.85–7.30 (Ar*H*); ^{13}C gel phase NMR (125 MHz, $CDCl_3$) δ 29.8, 30.5, 40.6, 44.5, 46.3, 55.4, 61.9, 67.4, 70.1, 70.8, 71.3, 72.7, 77.2, 77.5, 78.2, 79.3, 114.3, 125.7, 128.4, 133.5, 137.7, 145.4, 156.8; IR (neat) 3030–2865 (C–H), 1601, 1509, 1492, 1452, 1350, 1244, 1101, 697 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl-*para*-anisole 31. To brominated resin **30** (20.0 g, LL = 880 μmolg^{-1}, 17.6 mmol) swollen in a minimum of acetonitrile (200 mL) was added germylphenol **8e** (19.4 g, 81.2 mmol), tetra-*n*-butylammonium iodide (740 mg, 2.00 mmol) and caesium carbonate (26.2 g, 74.3 mmol) and the resulting mixture heated at 85 °C for 20 h. The reaction mixture was cooled and the resin was washed successively with MeCN (3 × 350 mL), DMF (3 × 350 mL), THF–water (1 : 1, 3 × 350 mL), THF (3 × 350 mL), MeOH (3 × 350 mL) and then dried *in vacuo* to give resin **31** as light brown granules (13.4 g, 74% conversion by the weight increase of the resin and the amount of phenol returned, LL = 0.52 mmol g^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 1.15–1.65 [C*H*(Ar)C*H*$_2$], 1.65–2.10 [ArC*H*$_2$, C*H*(Ar)C*H*$_2$], 2.37 (s, ArC*H*$_3$), 2.70–2.80 (GeC*H*$_2$), 3.50–4.15 (OC*H*$_3$, OC*H*$_2$), 6.10–6.70 (Ar*H*), 6.70–7.30 (m, Ar*H*), 7.41 (d, J = 4.5, Ar*H*); ^{13}C gel phase NMR (75 MHz, d_8-THF) δ 17.6, 21.8, 31.7, 37.4, 41.6, 71.7, 72.2, 128.9; IR (neat) 3030–2865 (C–H), 1593, 1510, 1494, 1453, 1281, 1245, 698 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl chloride 32. To germyl-*p*-anisole resin **31** (13.1 g, LL = 0.52 mmol g^{-1}, 6.8 mmol) swelled in CH_2Cl_2 (50 mL) was added HCl (65 mL, 1.0 M, 65 mmol) in Et_2O and the reaction mixture left to stir for 16 h. The solvent was then removed by filtration to give resin **32** as brown granules (11.7 g, 100% conversion by ^{1}H NMR, LL = 0.54 mmol g^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 1.00–2.30 [ArC*H*$_2$, C*H*(Ar)C*H*$_2$], 2.47 (s, ArC*H*$_3$), 2.85–2.95 (GeC*H*$_2$), 3.60–4.20 (OC*H*$_2$), 6.10–6.70 (Ar*H*), 6.70–7.30 (Ar*H*), 7.56 (d, J = 4.5, Ar*H*); IR (neat) 3030–2865 (C–H), 1601, 1509, 1493, 1452, 1243, 697 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl monothiophene (α-TBS) 33. A solution of LDA (1.11 mL, 2.0 M, 2.21 mmol) in hexanes–THF–ethylbenzene (6 : 5 : 3) was added dropwise to a degassed solution of silylthiophene **12** (616 mg, 2.18 mmol) in THF (4 mL) at −50 °C. This solution was warmed to −40 °C, stirred for 40 min at this temperature and recooled to −50 °C. The solution was then transferred by cannula to a degassed suspension of germylchloride resin **32** (777 mg, LL = 0.54 mmol g^{-1}, 0.42 mmol) in THF (10 mL) at −50 °C. The reaction mixture was stirred for 1 h at −40 °C, warmed to RT and stirred for a further 1 h. After quenching with sat. NH_4Cl (aq) (50 mL), the solvent was removed by filtration and the resin washed with DMF (50 mL × 3), THF : water 1 : 1 (50 mL × 3), THF (50 mL × 3) and MeOH (50 mL × 3). The resin was then dried *in vacuo* at 60 °C to give resin **33** as yellow/orange granules (876 mg, 83% conversion by weight increase of resin, LL = 0.40 mmol g^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 0.41 [s, Si(C*H*$_3$)$_2$], 0.91 (t, J = 4.5, CH$_2$C*H*$_3$), 0.95–2.30 [C(C*H*$_3$)$_3$, (C*H*$_2$)$_4$CH$_3$, ArC*H*$_2$CH$_2$Ge, C*H*(Ar)C*H*$_2$], 2.47 (s, ArC*H*$_3$), 2.54 [t, J = 5, C*H*$_2$(CH$_2$)$_4$CH$_3$], 2.80–2.95 (GeC*H*$_2$), 3.60–4.25 (OC*H*$_2$), 6.10–6.80 (Ar*H*), 6.80–7.30 (Ar*H*), 7.53 (d, J = 4.5, Ar*H*); IR (neat) 3030–2865 (C–H), 1601, 1509, 1492, 1451, 1244, 697 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl monothiophene (α-H) 34. To germylthiophene resin **33** (642 mg, LL = 400 μmolg^{-1}, 257 μmol) swollen in DMF (8 mL) was added caesium fluoride (341 mg,

2.24 mmol) and the mixture left to stir for 72 h at 110 °C. The solvent was then removed by filtration and the resin washed with DMF (2 × 75 mL), THF–H_2O (1 : 1, 3 × 75 mL), THF (3 × 75 mL) and MeOH (3 × 75 mL). The resin was then dried *in vacuo* at 60 °C to give germylthiophene resin **34** as brown granules (560 mg, 100% conversion by integrals in ^{1}H NMR, LL = 420 μmolg^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 0.82 (t, J = 7.0, CH_2CH_3), 0.85–2.20 [$(CH_2)_4CH_3$, $ArCH_2CH_2Ge$, $CH(Ar)CH_2$], 2.37 (s, $ArCH_3$), 2.48 [m, $CH_2(CH_2)_4CH_3$], 2.77 (m, $GeCH_2$), 3.60–4.15 (OCH_2), 6.10–7.30 (Ar*H*), 7.44 (d, J = 4.5, Ar*H*), 7.53 (m, S*CH*); IR (neat) 3030–2865 (C–H), 1601, 1508, 1492, 1451, 1242, 697 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl monothiophene (α-I) 35. A solution of LDA (315 μL, 2.0 M, 630 μmol) in hexanes–THF–ethylbenzene (6 : 5 : 3) was added dropwise to a suspension of germylthiophene resin **34** (526 mg, LL = 420 μmolg^{-1}; 221 μmol) in THF (4 mL) at −50 °C. After stirring for 2 h at −30 °C, a solution of degassed 1,2-diiodoethane (296 mg, 1.05 mmol) in THF (2 mL) was added by cannula at −50 °C. The resulting mixture was stirred in the dark for 2 h at −30 °C, warmed to RT and stirred for a further 1 h. The solvent was then removed by filtration and the resin washed with $Na_2S_2O_3$ (aq) (3 × 75 mL), THF–H_2O (1 : 1, 3 × 75 mL), THF (3 × 75 mL) and MeOH (3 × 75 mL). The resin was then dried *in vacuo* at 60 °C to give iodide resin **35** as orange grains (533 mg, 100% conversion by integrals of ^{1}H NMR, LL = 400 μmolg^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 0.82 (t, J = 4.5, CH_2CH_3), 0.85–2.20 [$(CH_2)_5CH_3$, $ArCH_2CH_2Ge$, $CH(Ar)CH_2$, $ArCH_3$], 2.77 (m, $GeCH_2$), 3.60–4.15 (OCH_2), 6.10–7.30 (Ar*H*), 7.42 (d, J = 7.0, Ar*H*); IR (neat) 3030–2865 (C–H), 1601, 1509, 1493, 1452, 1243, 697 (strong) cm^{-1}.

Quadragel®-di-*para*-tolylgermyl bithiophene (α-TBS) 36. To a degassed solution of boronic ester **16** (242 mg, 592 μmol), K_3PO_4 (134 mg, 985 μmol) and iodide resin **35** (493 mg, LL = 400 μmol g^{-1}, 197 μmol) swollen in DMF (4 mL) was added [$Pd(PPh_3)_4$] (11.6 mg, 10.0 μmol) and the resulting mixture stirred at 60 °C for 48 h. The solvent was then removed by filtration and the resin washed with DMF (2 × 50 mL), THF–H_2O (1 : 1, 3 × 50 mL), THF (3 × 50 mL) and MeOH (3 × 50 mL). The resin was then dried *in vacuo* at 60 °C to give bithiophene resin **36** as dark brown grains [508 mg, 87% conversion by mass of bithiophene **19** cleaved from the resin (see '3,4′-di-(*n*-hexyl)-[2,2′]bithiophenyl **19** *Method 2*', below), LL = 350 μmol g^{-1}]. ^{1}H MAS NMR ($CDCl_3$): δ 0.31 [s, $Si(CH_3)_2$], 0.75–2.50 [$C(CH_3)_3$, $(CH_2)_5CH_3$, $ArCH_2CH_2Ge$, $CH(Ar)CH_2$, $ArCH_3$], 2.80 (m, $GeCH_2$), 3.50–4.20 (OCH_2), 6.10–7.35 (Ar*H*), 7.47 (d, J = 7, Ar*H*); ^{13}C MAS NMR (100 MHz, $CDCl_3$) δ −4.5, 14.5, 17.3, 18.6, 21.9, 22.9, 23.0, 26.8, 29.6, 29.7, 30.0, 30.8, 31.1, 31.7, 32.0, 32.2, 40.9, 43.6, 67.9, 70.2, 71.1, 71.2, 115.0, 126.1, 128.4, 128.8, 129.1, 129.5, 133.6, 135.1, 137.4, 138.7, 139.3, 140.6, 141.5, 145.7, 151.4, 157.3; IR (neat) 3030–2865 (C–H), 1601, 1509, 1492, 1452, 1244, 697 (strong) cm^{-1}.

Double-couple procedure on Quadragel®-di-*para*-tolylgermyl bithiophene (α-TBS) 36. A solution of LDA (130 μL, 2.0 M, 260 μmol) in hexanes–THF–ethylbenzene (6 : 5 : 3) was added dropwise to a suspension of germylthiophene resin **36** (219 mg, LL = 350 μmol g^{-1}, 76.7 μmol) in THF (2 mL) at −50 °C. After stirring for 40 min at −40 °C, a solution of degassed 1,2-diiodoethane (124 mg, 440 μmol) in THF (1 mL) was added by cannula at −50 °C. The reaction mixture was stirred in the dark for 1 h at −40 °C, warmed to RT and stirred for a further 1 h. The solvent was then removed by filtration and the resin washed with $Na_2S_2O_3$ (aq) (3 × 50 mL), THF–H_2O (1 : 1, 3 × 50 mL), THF (3 × 50 mL) and MeOH (3 × 50 mL). The resin was then dried *in vacuo* at 60 °C to give brown grains (221 mg) which were then swollen in DMF (1.5 mL). To this swollen resin was added boronic ester **16** (96.0 mg, 235 μmol) and K_3PO_4 (37.2 mg, 273 μmol), the reaction mixture degassed and [$Pd(PPh_3)_4$] (4.5 mg, 3.89 μmol) added. The resulting mixture was stirred at 60 °C for 48 h. The solvent was then removed by filtration and the resin washed with DMF (2 × 50 mL), THF–H_2O (1 : 1, 3 × 50 mL), THF (3 × 50 mL) and MeOH (3 × 50 mL). The resin was then dried *in vacuo* at 60 °C to give bithiophene resin **36** as dark brown grains [196 mg, LL = 350 μmol g^{-1} by mass of bithiophene **19** cleaved from the resin (see '3,4′-di-(*n*-hexyl)-[2,2′]bithiophenyl **19** *Method 2*', below)]. Spectroscopic data as above.

Quadragel®-di-*para*-tolylgermyl bithiophene (α-H) 37. To germylthiophene resin **36** (165 mg, LL = 350 μmol g^{-1}, 578 μmol) swollen in DMF (2 mL) was added caesium fluoride (50.0 mg, 329 μmol) and the mixture left to stir for 72 h at 110 °C. The solvent was then removed by filtration and the resin washed with DMF (2 × 75 mL), THF–H_2O (1 : 1, 3 × 75 mL), THF (3 × 75 mL) and MeOH (3 × 75 mL). The resin was then dried *in vacuo* at 60 °C to give germylthiophene resin **37** as a dark brown beads (157 mg, ~100% conversion by integrals in ^{1}H NMR, LL = 360 μmol g^{-1}). ^{1}H MAS NMR (400 MHz, $CDCl_3$): δ 0.75–2.50 [$(CH_2)_5CH_3$, $ArCH_2CH_2Ge$, $CH(Ar)CH_2$, $ArCH_3$], 2.80 (m, $GeCH_2$), 3.50–4.15 (OCH_2), 6.10–7.40 (Ar*H*), 7.47 (d, J = 6.5, Ar*H*); IR (neat) 3030–2865 (C–H), 1601, 1508, 1492, 1451, 1243, 697 (strong) cm^{-1}.

General procedure D

TFA mediated cleavage of 3,4′-di-(*n*-hexyl)-[2,2′]bithiophene **19**[54] from resin 36 (Method 1).

3,4′-Di-(*n*-hexyl)-[2,2′]bithiophene 19[54] from mono-coupled resin 36. To bithiophene resin **36** (35.7 mg, 14.3 μmol) was added a 33% v/v solution of TFA in CH_2Cl_2 (750 μL) and the mixture left to stir at RT for 2 h. The solvent was then removed by filtration and the resin washed with CH_2Cl_2 (3 × 50 mL). These washings were then passed through a plug of silica and concentrated *in vacuo* to give bithiophene **19** as a yellow oil [3.1 mg, >94.0% pure by HPLC: Jupiter ODS-C18 column (250 × 0.46 cm), UV 254 nm detection, 1 mL min^{-1}, 5 → 100% MeCN in H_2O + 0.1% formic acid, R_t = 17.1 min.]. R_f 0.60 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.34 (s, 9H), 0.84–0.92 (6H), 1.20–1.35 (12H), 1.52–1.70 (4H), 2.63 (t, J = 8.5, 2H), 2.74 (t, J = 8, 2H), 6.90 (d, J = 5.5, 1H), 7.03 (s, 1H), 7.12 (d, J = 5.5, 1H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 14.1 (q, 2C), 22.6 (t), 29.0 (t), 29.1 (t), 29.2 (t), 29.7 (t), 30.4 (t), 30.5 (t), 30.7 (t), 31.6 (t), 31.7 (t), 119.9 (s), 123.4 (s), 127.3 (s), 129.9 (s), 130.9 (d), 135.8 (d), 139.3 (d), 143.5 (d); IR (neat) 2950–2850 (C–H), 1457, 1377 cm^{-1}; MS (EI+) m/z 334 (M^+); HRMS calcd. for $C_{20}H_{30}S_2$ (M^+) 334.1789, found 334.1784.

3,4′-Di-(*n*-hexyl)-[2,2′]bithiophene 19[54] from double-coupled resin 36. According to the general procedure D, bithiophene resin **36** (40.4 mg, 16.2 μmol) in TFA in CH_2Cl_2 (750 μL) gave bithiophene

19 as a yellow oil [6.1 mg, >96.0% pure by HPLC (same conditions and R_t as above)]. Spectroscopic data as above.

HypoGel®-Br 39. To a suspension of HypoGel® **38** (24.55 g, LL = 0.80 mmol g^{-1}, 19.6 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added triphenylphosphine (10.30 g, 39.3 mmol) and carbon tetrabromide (26 g, 78.4 mmol). The reaction mixture was stirred at RT under N_2 for 24 h. After removal of the solvent by filtration, the resin was washed with DMF (300 mL), THF–water (1 : 1) (2 × 300 mL), THF (2 × 300 mL) and MeOH (2 × 300 mL) and was dried for 16 h at 50 °C *in vacuo* to give the brominated resin **39** as pale yellow granules (25 g, 100% conversion by ^{13}C NMR, LL = 0.80 mmol g^{-1}). ^1H MAS NMR (400 MHz, $CDCl_3$): δ 1.00–1.75 [C*H*(Ar)CH_2], 1.15–1.60 [C*H*(Ar)CH_2], 1.60–2.10 [C*H*(Ar)CH_2], 3.50–3.60 (OCH_2), 3.60–3.90 (CH_2CH_2O), 6.20–6.80 (Ar*H*), 6.80–7.30 (Ar*H*); ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 31.7, 32–56, 71.7, 72.3, 120–135, 146.3 ppm; IR (neat) 3030–2865 (C–H), 1601, 1493, 1452, 1349, 1296, 1249, 1101 (strong) cm^{-1}; Anal. C, 76.5%, H 7.7%, Br 6.4%.

HypoGel®-di-*para*-tolylgermyl-*para*-anisole 40. Germylphenol **8e** (17.8 g, 36.8 mmol), tetra-*n*-butylammonium iodide (680 mg, 1.84 mmol) and cesium carbonate (19.5 g, 55.2 mmol) were added to a suspension of brominated resin **40** (24.5 g, LL = 0.80 mmol g^{-1}, 18.4 mmol) in acetonitrile (150 mL). This mixture was stirred at 85 °C for 22 h. After removal of the solvent by filtration, the resin was washed extensively with acetonitrile (3 × 300 mL), DMF (2 × 300 mL), THF–water (1 : 1) (3 × 300 mL), THF (2 × 300 mL), MeOH (2 × 300 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **40** as pale yellow granules (29.0 g, 99% conversion by the amount of germylphenol returned and Ge elemental, LL = 0.48 mmol g^{-1}). ^1H MAS NMR (400 MHz, $CDCl_3$): δ 1.00–1.65 [C*H*(Ar)CH_2], 1.65–2.10 [ArCH_2CH$_2$Ge, C*H*(Ar)CH_2)], 2.37 (s, ArCH_3), 2.80 (m, GeCH_2), 3.40–4.15 (OCH_3, CH_2CH_2O), 6.10–6.70 (Ar*H*), 6.70–7.30 (Ar*H*), 7.41 (d, J = 6.5, Ar*H*); ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.6, 21.8, 31.4, 36–52, 55.4, 69.0, 70.8, 71.7, 114.9, 115.3, 128.6, 129.5, 129.9, 135.0, 135.8, 137.0, 139.3, 161.7 ppm; IR (neat) 3030–2865 (C–H), 1593, 1509, 1493, 1452, 1349, 1281, 1245, 1102 (strong), 698 (strong) cm^{-1}; Anal. C 78.0%, H 7.7%, Ge 3.5%.

HypoGel®-di-*para*-tolylgermyl chloride 41. A solution of 1 M HCl in diethyl ether (150 mL, 150 mmol) was added to a suspension of resin **40** (27.0 g, LL = 0.48 mmol g^{-1}, 14.9 mmol) in CH_2Cl_2 (500 mL). This mixture was stirred at RT under N_2 for 20 h. After removal of the solvent by filtration, the resin was washed with anhydrous diethyl ether (2 × 200 mL) and dried at 50 °C *in vacuo* for 16 h to give resin **41** as pale yellow granules (25.0 g, 100% conversion by ^1H NMR, LL = 0.49 mmol g^{-1}). ^1H MAS NMR (400 MHz, $CDCl_3$): δ 1.20–2.20 [ArCH_2CH$_2$Ge, C*H*(Ar)CH_2], 2.38 (s, ArCH_3), 2.90 (m, GeCH_2), 3.40–4.20 (CH_2CH_2O), 6.10–6.70 (Ar*H*), 6.70–7.30 (Ar*H*), 7.49 (d, J = 7, Ar*H*); ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 21.8, 22.0, 30.2, 36–52, 69.0, 70.7, 71.7, 115.4, 129.7, 130.2, 133.6, 134.4, 136.3, 141.1, 158.4 ppm; IR (neat) 3030–2865, 1601, 1510, 1493, 1452, 1349, 1245, 1102 (strong), 607 (strong) cm^{-1}; Anal. C 76.7%, H 7.9%, Cl 2.2%, Ge 3.6%.

HypoGel®-di-*para*-tolylgermyl mono(triarylamine) (*p*-OTBS) 43. A solution of *n*-butyllithium (2.5 M in hexane) (3.4 mL, 5.4 × 10^{-3} mol) was added dropwise to a solution of triaryl bromide **42**[27] (2.53 g, 5.4 mmol) in THF (20 mL) at −78 °C. After being stirred for 45 min, the mixture was transferred by cannula to a suspension of resin **41** (3.00 g, LL = 0.49 mmol g^{-1}, 1.5 mmol) in toluene (30 mL) at −78 °C. The resulting mixture was stirred for 18 h at RT. An aqueous solution of 1 M HCl was then added and the mixture stirred another 30 min. After removal of the solvent by filtration, the resin was washed extensively with DMF (75 mL), THF–water (1 : 1) (2 × 75 mL), THF (2 × 75 mL), MeOH (2 × 75 mL) and was dried for 18 h at 50 °C *in vacuo* to give resin **43** as pale yellow granules (3.23 g, LL = 0.37 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ −4.1, 17.5, 19.0, 21.1, 21.7, 26.3, 31.4, 36–52, 69.0, 70.8, 71.7, 115.33, 121.65, 125.60, 128.02, 129.81, 130.81, 133.37, 135,35, 135.83, 136.48, 139.23, 142.28, 146.33, 150.19, 153.09 ppm; Anal. C, 80.2%; H, 8.0%; N, 0.5%; Ge, 2.7%.

HypoGel®-di-*para*-tolylgermyl mono(triarylamine) (*p*-OH) 44. TBAF (1.34 g, 4.25 mmol) was added to a suspension of resin **43** (2.43 g, LL = 0.37 mmol g^{-1}, 1.22 mmol) in THF (20 mL). This mixture was stirred under N_2 at RT for 20 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (75 mL), THF–water (1 : 1) (2 × 75 mL), THF (2 × 75 mL), MeOH (2 × 75 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **44** as pale yellow granules (2.33 g, LL = 0.38 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.5, 21.1, 21.8, 31.5, 36–52, 68.5, 70.8, 71.7, 115.33, 117.29, 121.08, 125.13, 128.92, 129.80, 130.63, 132.86, 135.35, 135.85, 139.17, 146.53, 150.42, 156.54 ppm; Anal. C, 80.8%; H, 7.7%; N, 0.7%; Ge, 2.8%.

HypoGel®-di-*para*-tolylgermyl mono(triarylamine) (*p*-OTf) 45. Trifluoromethanesulfonic anhydride (0.50 mL, 2.97 mmol) was added slowly to a suspension of resin **44** (1.61 g, LL = 0.38 mmol g^{-1}, 0.81 mmol) swollen in pyridine (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min, then allowed to warm to RT and stirred at this temperature for a further 16 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (75 mL), THF–water (1 : 1) (2 × 75 mL), THF (2 × 75 mL), MeOH (2 × 75 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **45** as pale yellow granules (1.73 g, LL = 0.37 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.5, 21.2, 21.8, 31.4, 36–52, 68.5, 70.8, 71.7, 115.25, 117.84, 123.08, 124.39, 127.14, 129.84, 131.35, 132.72, 135.83, 136.97, 139.09, 145.44, 146.82, 148.97 ppm; ^{19}F gel-phase NMR (75 MHz, d_8-THF) δ −76.4 ppm; Anal. C, 76.3%; H, 6.7%; N, 0.7%; S, 1.3%; F, 2.2%; Ge, 2.7%; N, 0.7%.

HypoGel®-di-*para*-tolylgermyl di(triarylamine) (*p*-OTBS) 46. Resin **45** (1.34 g, LL = 0.37 mmol g^{-1}, 0.67 mmol), triarylamine boronic ester **4** (1.73 g, 3.35 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), aqueous Na_2CO_3 (2 M, 10 mL) in 1,2-DME (10 mL) were stirred at 80 °C for 18 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (50 mL), THF–water (1 : 1) (2 × 50 mL), THF (2 × 50 mL), MeOH (2 × 50 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **46** as dark brown granules (1.25 g, LL = 0.34 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ −4.0 (b), 17.5 (b), 19.0 (b), 21.6 (b), 26.4 (b), 31.5 (b), 36–52, 71.6 (b), 110.1 (b), 129.7 (b), 135.40 (b), 146.5 (b) ppm; Anal. C, 77.1%; H, 7.0%; N, 1.0%; Ge, 2.5%.

HypoGel®-di-*para*-tolylgermyl di(triarylamine) (*p*-OH) 47. TBAF (0.74 g, 2.35 mmol) was added to a suspension of resin **46** (0.94 g, LL = 0.34 mmol g^{-1}, 0.47 mmol) in THF (10 mL).

This mixture was stirred under N_2 at RT for 20 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (30 mL), THF–water (1 : 1) (2 × 30 mL), THF (2 × 30 mL), MeOH (2 × 30 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **47** as dark brown granules (0.91 g, LL = 0.33 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.5 (b), 21.8 (b), 31.5 (b), 36–52, 71.6 (b), 110.1 (b), 115–117 (b), 129.8 (b), 135.6 (b), 146.0 (b) ppm; Anal. C, 78.5%; H, 7.0%; N, 1.0%; Ge, 2.4%.

HypoGel®-di-*para*-tolylgermyl di(triarylamine) (*p*-OTf) 48. Trifluoromethanesulfonic anhydride (0.30 mL, 1.75 mmol) was added slowly to a suspension of resin **47** (0.70 g, LL = 0.33 mmol g^{-1}, 0.35 mmol) swollen in pyridine (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min, then allowed to warm to RT and stirred at this temperature for a further 16 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (30 mL), THF–water (1 : 1) (2 × 30 mL), THF (2 × 30 mL), MeOH (2 × 30 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **48** as brown granules (0.65 g, LL = 0.30 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.5 (b), 21.9 (b), 31.4 (b), 36–52, 71.7 (b), 113.9 (b), 115.2 (b), 126.4 (b), 129.4 (b), 135.5 (b), 145.9 (b) ppm; ^{19}F gel-phase NMR (75 MHz, d_8-THF)) δ −74.6 ppm; Anal. C, 67.9%; H, 6.3%; N, 1.1%; S, 1.1%; F, 1.8%; Ge, 2.2%.

HypoGel®-di-*para*-tolylgermyl tri(triarylamine) (*p*-Me) 49. Resin **48** (0.53 g, LL = 0.30 mmol g^{-1}, 0.35 mmol), triarylamine boronic ester **5** (1.73 g, 3.35 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), aqueous Na_2CO_3 (2 M, 5 mL) in 1,2-DME (5 mL) were stirred at 80 °C for 18 h. After removal of the solvent by filtration, the resin was washed extensively with DMF (30 mL), THF–water (1 : 1) (2 × 30 mL), THF (2 × 30 mL), MeOH (2 × 30 mL) and was dried for 16 h at 50 °C *in vacuo* to give resin **49** as brown granules (0.41 g, LL = 0.30 mmol g^{-1}). ^{13}C gel-phase NMR (75 MHz, d_8-THF) δ 17.5 (b), 21.0 (b), 22.5 (b), 31.4 (b), 36–52, 71.7 (b), 115.3 (b), 125.5 (b), 128.1 (b), 129.8 (b), 130.9 (b), 133.1 (b), 135.4 (b), 136.6 (b), 146.5 (b) ppm; Anal. C, 72.3%; H, 6.2%; N, 1.3%; Ge, 2.2%.

***N*4′-[4′-(Di-*para*-tolylaminobiphenyl-4-yl]-*N*4-(4′-phenyl)-*N*4, *N*4′-di-*para*-tolylbiphenyl-4,4′-diamine 50.** A suspension of resin **49** (0.33 g, LL = 0.30 mmol g^{-1}, 0.10 mmol) in trifluoroacetic acid (10% in CH_2Cl_2) (5 mL) was stirred at RT for 16 h. The resin was separated off by filtration and washed with CH_2Cl_2. The organic washings were concentrated 50 °C *in vacuo* to give a dark brown oil. The crude material was purified by FC (hexane–ethyl acetate, 10 : 1) to give the expected product as a white solid [0.07 g, 90%, >97% pure by HPLC: Jupiter ODS-C18 column (250 × 0.46 cm), UV 300 nm detection, 1 mL min^{-1}, 5 → 100% MeCN in H_2O + 0.1% formic acid, R_t = 9.7 min.]. ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 6H), 2.31 (s, 3H), 2.32 (s, 3H), 6.95–7.12(m, 27H), 7.21–7.24 (m, 2H), 7.39–7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.82, 20.85, 20.87, 122.37, 122.90, 123.57, 123.68, 123.78, 124.58, 125.05, 125.10, 127.12, 127.20, 127.22, 129.16, 129.88, 129.97, 130.00, 132.47, 132.89, 132.99, 133.87, 134.40, 134.51, 134.67, 145.05, 145.15, 145.33, 146.64, 146.75, 146.89, 147.15, 147.93 ppm; HRMS (EI+) calcd. for $C_{58}H_{49}N_3$ (M^+) 787.3926; found 787.3923.

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References

1 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402–428.
2 C. D. Dimititrakopoulos and D. J. Mascaro, *IBM J. Res. Dev.*, 2001, **45**, 11–27.
3 C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077–1086.
4 H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, 2001, **34**, 359–369.
5 R. D. McCullough, *Adv. Mater.*, 1998, **10**, 1–24.
6 J. G. Laquindanum, H. E. Katz and A. J. Lovinger, *J. Am. Chem. Soc.*, 1998, **120**, 664–672.
7 A. Donat-Bouillud, I. Levesque, Y. Tao, M. D'Iorio, S. Beaupre, P. Blondin, M. Ranger, J. Bouchard and M. Leclerc, *Chem. Mater.*, 2000, **12**, 1931–1936.
8 J. V. Allen, J. Fergus, S. W. Leeming, J. D. Morgan and M. Thomas, *WO99/35537*, 1999, Avecia Ltd.
9 S. W. Leeming, J. Veres, J. D. Morgan, E. Wright and B. A. Brown, *WO01/68740*, 2001, Avecia Ltd.
10 M. J. Plater and T. Jackson, *Tetrahedron*, 2003, **59**, 4687–4692 and references therein.
11 C. A. Briehn, T. Kirschbaum and P. Bäuerle, *J. Org. Chem.*, 2000, **65**, 352–359.
12 W. Li, T. Maddux and L. Yu, *Macromolecules*, 1996, **29**, 7329–7334.
13 G. Bidan, A. De Nicola, V. Enee and S. Guillerez, *Chem. Mater.*, 1998, **10**, 1052–1058.
14 P. Bäuerle, *Handbook of Oligo- and Polythiophenes*, ed. D. Fichou, Wiley-VCH,Weinheim, 1999.
15 J. P. Sadighi, R. A. Singer and S. L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 4960–4976.
16 F. E. Goodson, S. I. Hauck and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 7527–7539.
17 J. Louie and J. F. Hartwig, *Macromolecules*, 1998, **31**, 6737–6739.
18 P. R. L. Malenfant and J. M. J. Fréchet, *Chem. Commun.*, 1998, 2657–2658.
19 S. Huang and J. M. Tour, *J. Org. Chem.*, 1999, **64**, 8898–8906.
20 T. Kirschbaum, C. A. Briehn and P. Bäuerle, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1211–1216.
21 T. Kirschbaum and P. Bäuerle, *Synth. Met.*, 2001, **119**, 127–128.
22 C. A. Briehn, M.-S. Schiedel, E. M. Bonsen, W. Schuhmann and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2001, **40**, 4680–4683.
23 C. A. Briehn and P. Bäuerle, *J. Comb. Chem.*, 2002, **4**, 457–469.
24 C. A. Briehn and P. Bäuerle, *Chem. Commun.*, 2002, 1015–1023.
25 K. Burgess, *Solid-Phase Organic Synthesis*, Wiley, New York, 2000.
26 A. C. Spivey, D. J. Turner, M. L. Turner and S. Yeates, *Org. Lett.*, 2002, **4**, 1899–1902.
27 R. Anemian, D. C. Cupertino, P. R. Mackie and S. Yeates, *Tetrahedron Lett.*, 2005, **46**, 6717–6721.
28 Part of the work described here relating to the development of the SPS of oligo-(3-alkylthiophene)s has been published in preliminary form (ref. 38).
29 M. J. Plunkett and J. A. Ellman, *J. Org. Chem.*, 1997, **62**, 2885–2893.
30 A. C. Spivey, C. M. Diaper and A. J. Rudge, *Chem. Commun.*, 1999, 835–836.
31 A. C. Spivey, C. M. Diaper, H. Adams and A. J. Rudge, *J. Org. Chem.*, 2000, **65**, 5253–5263.
32 J. Clayden, *Organolithiums: Selectivity for Synthesis*, Pergamon, Oxford, 2002.
33 A. de Meijere and F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, New York, 2004.

34 D. Prim, J. M. Campagne, D. Joseph and B. Andrioletti, *Tetrahedron*, 2002, **58**, 2041–2075.
35 A. C. Comley and S. E. Gibson, *Angew. Chem., Int. Ed.*, 2001, **40**, 1012–1032.
36 S. Brase and S. Dahmen, *Chem.–Eur. J.*, 2000, **6**, 1899–1905.
37 A. C. Spivey, C. J. G. Gripton, C. Noban and N. J. Parr, *Synlett*, 2005, 2167–2170.
38 A. C. Spivey, D. J. Turner, M. L. Turner and S. Yeates, *Synlett*, 2004, 111–115 and references therein.
39 The synthesis of this germyl model system has been described previously (ref. 38). The ethoxy ethyl group was incorporated to act as a surrogate for a PEG grafted resin.
40 D. J. Turner, *PhD Thesis*, 2003, University of Sheffield. The synthesis of **2c** is compromised particularly by low levels of impurities generated during the bromine-lithium exchange/TBS chloride quenching reaction.
41 W. Haubold, J. Herdtle, W. Gollinger and W. Einholz, *J. Organomet. Chem.*, 1986, **315**, 1–8.
42 M. J. Sharp, W. Cheng and V. Snieckus, *Tetrahedron Lett.*, 1987, **28**, 5093–5096.
43 D. Kaufman, *Chem. Ber.*, 1987, **120**, 853–854.
44 D. Kaufman, *Chem. Ber.*, 1987, **120**, 901–905.
45 U. Gross and D. Kaufman, *Chem. Ber.*, 1987, **120**, 991–994.
46 Z. Z. Song, Z. Y. Zhou, T. C. W. Mak and H. N. C. Wong, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 432–434.
47 G. M. Farinola, V. Fiandanese, L. Mazzone and F. Naso, *J. Chem. Soc., Chem. Commun.*, 1995, 2523–2524.
48 E. Hupe, M. I. Calaza and P. Knochel, *Chem. Commun.*, 2002, 1390–1391.
49 Z. Zhao and V. Snieckus, *Org. Lett.*, 2005, **7**, 2523–2526.
50 A. C. Spivey, R. Srikaran, C. M. Diaper and D. J. Turner, *Org. Biomol. Chem.*, 2003, **1**, 1638–1640.
51 W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals, 5th edn.*, Butterworth-Heinmann, Boston, 2003.
52 M. Bouachrine, J. Lere-Porte, J. J. E. Moreau and M. W. C. Man, *J. Mater. Chem.*, 1995, **5**, 797–799.
53 P. G. Maslov and A. A. Klochikhin, *Zh. Obshch. Khim.*, 1958, **28**, 835–838.
54 D. S. Galvao, D. A. Dos Santos, B. Laks and M. C. Dos Santos, *Synth. Met.*, 1991, **43**, 3521–3526.