Preparation of Conjugated Gels of Regioregular HT Sexi(3-*n*-octylthiophene) and Related Star Molecules

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We present new kinds of conducting gels of octylthiophene. Contrary to the gels previously obtained in our laboratory, they present two "high" gelation thresholds (i.e., related to high crosslink ratios). Consequently, systems close to the gelation threshold can be prepared with accuracy. Furthermore, they are calibrated and regioregular: The length and the regioregularity of the chain segments between adjacent cross-links are fully controlled. They are prepared by chemical polycondensation of monodisperse regioregular [(head-to-tail (HT)] oligo(octylthiophene)s with tribromobenzene. For the preparation of these gels, two kinds of regioregular oligomers are synthesized: linear (from dimer to hexamer) and "star" oligo(octylthiophene)s. The two star oligomers are made of a benzene ring trisubstituted in meta positions by a regioregular (HT) segment of respectively six (E6) and twelve (E12) octylthiophenes. The structural properties of the oligomers are studied by ^{1}H and ^{13}C NMR spectroscopy; information concerning their conformation is reported. The optical properties (UV−vis absorption and fluorescence) of the star oligomers are compared with that of the linear oligomers. A linear evolution of the energy of the fluorescence transitions of the linear regioregular oligo(octylthiophene)s with the reverse of thiophene number is demonstrated for the first time. The Stille coupling chosen to prepare the gels from the oligomers is studied to determine the experimental conditions allowing both the good solubility of large clusters formed during the gel preparation and the good yield of the coupling reaction. A first series of 14 networks is reported. It is characterized by two gelation thresholds that are very high, as expected, but very close one from another. A strategy is proposed to increase the distance between the two gelation thresholds in the coming series.

Introduction

Recently a new class of conducting systems has emerged: conducting gels. They have immediately attracted a great deal of scientific interest[1−8] for several reasons: (a) They present an unusual combination of properties: the specific gel deformation properties (swelling, high elasticity) and the transport properties of the conducting polymers; (b) the interplay between electronic energy and conformational entropy may lead to coupled effects including elasticity, swelling, and conductivity. Therefore, these systems are expected to present an electromechanical responsive behavior (a small variation of conductivity may result in a large deformation of the system and vice versa); (c) they may be very interesting for the study of the fundamental processes of conductivity in polymeric systems: in the swollen state, the chains are well separated one from another, contrary to what happens in "classical" one-dimensional conducting polymers in the solid state. In this case the electronic transport must follow the paths of the network. Therefore the conductivity is expected to depend directly on the statistical structure, and its law of variation with the structurally relevant variable should reflect the state of gelation.[9]

A polymer gel is a three-dimensional macromolecular network made of chain segments connected by cross-links. Such systems are complex because their structure

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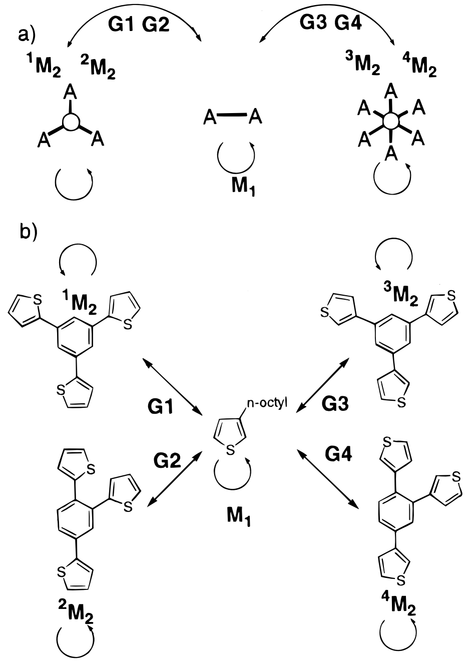
Scheme 1. A and B Are Chemical Functions: (a) Schematic Way of Preparation of Gels G1 to G4 and (b) Preparation of Each Series G*i* of Gels ($1 \leq i \leq 4$) by Reaction of Cross-Link $^iM_2$ with M_1



For each series, $0.003 \leq R \leq 0.15$; the arrow ↷ indicates that the molecule can react with itself; the arrow ↔ indicates the reaction between M_1 and $^iM_2$.

depends on their conditions of preparation. Most of the conducting gels reported in the literature have been obtained from the uncontrolled gelation of classical linear conducting polymers solutions.[2,3a,4] That is the reason the nature and the density of the cross-links are not determined. To our knowledge, only few well-defined gels prepared from well-defined small molecules have been reported until now: they are either not fully conjugated[5] or cannot be doped or swollen[6] or have not been extensively studied.[7,8] Furthermore, their statistical structures have not been explored.

We already reported the preparation of four series G1, G2, G3 and G4 of well-defined conducting gels of poly(3-*n*-octylthiophene) prepared from well-characterized small molecules (monomers). They were obtained by oxidative copolymerization of a bifunctional monomer (M_1) with four different cross-links ($^1M_2$, $^2M_2$, $^3M_2$, and $^4M_2$) that were either tri- or hexafunctional[10] (Scheme 1a). We stress the fact that in this case each monomer M_1 or $^iM_2$ ($1 \leq i \leq 4$) could react both with itself and with the other one. Each series was related to a specific cross-link ($^iM_2$, $1 \leq i \leq 4$). The bifunctional monomer M_1 was the 3-*n*-octylthiophene. The cross-links were four different trithienyl benzenes we prepared and characterized[10a] (see Scheme 1b). Each gel of a series corresponded to a specific value of the cross-link ratio *r* defined as:

$$r = (f_{^iM_2} \times n_{^iM_2})/(f_{^iM_1} \times n_{^iM_1}) \qquad (1)$$

where $f_{^iM_j}$ is the functionality of the molecule ^iM_j and $n_{^iM_j}$ the number of moles of ^iM_j. The statistical structure of these networks was explored.[11] The evolution of their specific properties (such as gel fraction, swelling ratio, proton NMR relaxation rate) described master curves as a function of the relevant structural variable that was determined. This variable could be directly related to the distance to the threshold predicted within the mean field theory using the analogy between the sol gel transition and the percolation model. In the systems prepared by this route, the gelation point was related to a very low ratio *r* ($r \leq 0.003$), the length of the poly(octylthiophene) chain segment between two adjacent potential cross-links was only known in the average and their regioregularity was uncontrolled. This latter structural parameter has to be taken into account because the steric hindrance due to the alkyl chains may have a dramatic effect on the conductivity.[12] The transport properties,[13] the diffusion properties,[14] and the NMR relaxation properties[11] of these gels were reported.

The gels we now plan to obtain are prepared by the chemical polycondensation of a trifunctional cross-link M_2 with either a bifunctional monomer $^1M_1$ (series CG1) or trifunctional monomers $^2M_1$ and $^3M_1$ (respectively corresponding to the series CG2 and CG3) (see Scheme 2a). We stress the fact that the condensation exclusively occurs between the monomer and the cross-link. The cross-link M_2 is a 1,3,5-trifunctionalized benzene (see Scheme 2b). The bifunctional monomer $^1M_1$ of the series CG1 is the monodisperse regioregular head-to-tail (HT) hexa(octylthiophene) (**L6**). The trifunctional monomers of the series CG2 and CG3 (respectively $^2M_1$ and $^3M_1$) are star molecules made of a benzene ring substituted in 1,3,5 positions by respectively three HT regioregular hexa(octylthiophene)s(**E6**) and three HT regioregular dodeca(octylthiophene)s (**M12**). The monomers $^1M_1$(**L6**), $^2M_1$ (**E6**), and $^3M_1$(**E12**) are presented on Scheme 2b. These new gels of poly(octylthiophene) present several significant differences with the gels previously obtained (G1 to G4): (a) Two gelation thresholds are expected that are respectively related to either an excess of the cross-links M_2 or of the monomers $^iM_1$; (b) the gelation points are expected to be related to higher *r* values than those of the gels obtained by oxidative copolymerization. This may be of great interest to get systems close to the gelation thresholds with accuracy (c) the length and the regioregularity of the poly(octylthiophene) segment between two adjacent potential cross-links are fully controlled.

The first part of this paper is devoted to the synthesis of the kit of elementary units ($^1M_1$ = **L6**,$^2M_1$ = **E6**, and $^3M_1$ = **E12**) and to the preparation of the first series of gels (CG1). We report an improved step-by-step preparation of the linear oligo(octylthiophene)s **Ln** ranging from the dimer **L2** to the hexamer[15] **L6**. We also report

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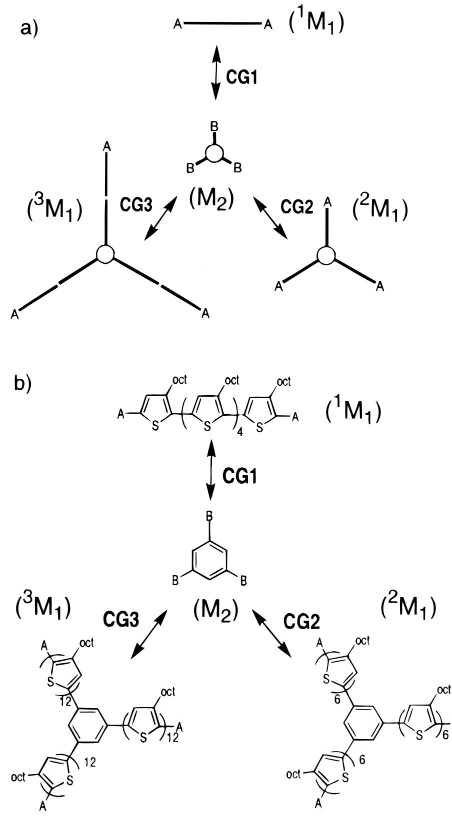
Scheme 2. A and B Are Chemical Functions: (a) Schematic Way of Preparation of Three Series CG1, CG2, and CG3 and (b) Detailed Preparation of Each Series of Gels CG1, CG2, and CG3



Arrow ↔ indicates the reaction between M$_2$ and ^{i}M$_1$.

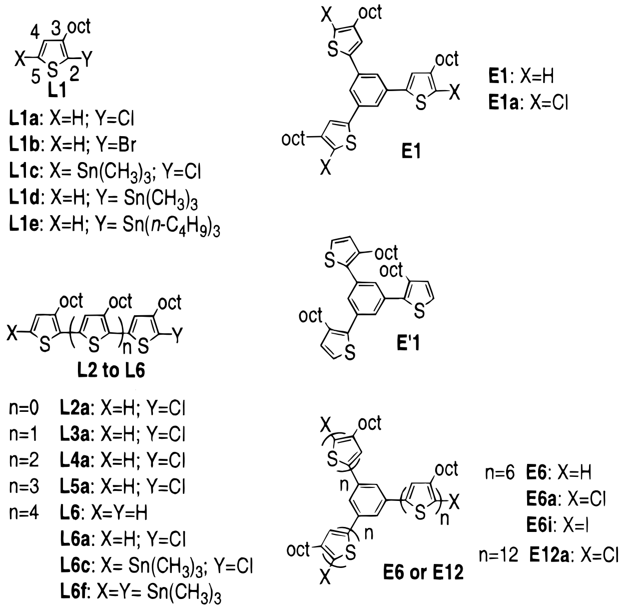
the study of the Stille coupling used to prepare gels from the starting units ^{i}M$_1$ and M$_2$. The experimental conditions allowing both the good solubility of large clusters formed during the gel preparation and the good yield of the reaction are determined on the basis of this study. The second part of this paper deals with the study of structural and optical properties of the elementary units. The properties of the star oligomers are compared with that of the linear oligomers.

Results and Discussion

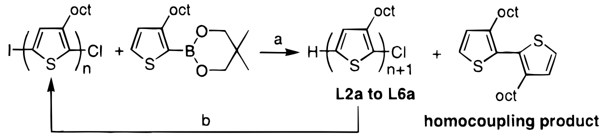
All the molecules synthesized in this work are numbered according to Schemes 3 and 6.

Preparation of Linear Oligomers L2a to L6a and L6 (^{1}M$_1$). A full control of the regioregularity of **L6** (^{1}M$_1$: 3,4′,4″,4‴,4⁗,4′′′′′-sexioctyl-2,2′:5′,2″:5″-2‴:3‴,2⁗:5⁗-2′′′′′-sexithiophene) required a step-by-step synthesis from the monomer to the hexamer. The synthesis was performed according to the procedure published by one of us.[15] Each step consisted of a Suzuki coupling reaction[16] between the boron-functionalized 3-octylthiophene and the iodinated and chlorinated oligomer of n octylthiophenes ($1 \leq n \leq 5$) obtained at the previous step (Scheme 4). In the present work, efforts were directed toward the optimization of the synthetic procedure by avoiding as much as possible the homocoupling side reaction of the boronate. The byproduct

Scheme 3. Linear and Star-Shaped Molecules Synthesized: Description and Nomenclature



Scheme 4. Synthesis of the Linear Oligomers L2A–L6A ($0 \leq n \leq 5$)



(a) 1,2-Dimethoxyethane, Pd(PPh$_3$)$_3$, aq. NaHCO$_3$, reflux; (b) chloroform/acetic acid 50/50 vol., I$_2$, Hg(Oac)$_2$.

resulting from the homocoupling of the boronate was formed up to 10% with respect to the expected oligomer, according to HPLC. The yield with regard to the iodinated oligomer before purification was not affected because the boronate was present in a large excess (20% with respect to the iodinated oligomer). But this yield was affected after purification when the expected oligomer and the homocoupling product were difficult to separate. This was mainly true in the case of the dimer **L2a**. It was then important to decrease the homocoupling reaction yield to increase the yield in **L2a** after purification and consequently the final yield in **L6a**. This homocoupling reaction was mainly due to the presence of oxygen[17] in the reaction mixture and to partial oxidation of the commercial catalyst Pd(PPh$_3$)$_4$ before use. By using freshly prepared catalyst[18] Pd(PPh$_3$)$_3$ in a thoroughly degassed mixture, the yield of the coupling step (**L1a → L2a)** was increased from 80 to 95%. In the same time, the amount of the homocoupling product was decreased from 10 to 4% with respect to **L2a**. It was not possible to decrease the amount of the homocoupling product beyond 4%. One reason could be that a complete degassing was difficult to achieve because the reaction was performed on a large scale. Using this optimized procedure, 8 g of the hexamer **L6a** were prepared in 30% yield (with respect

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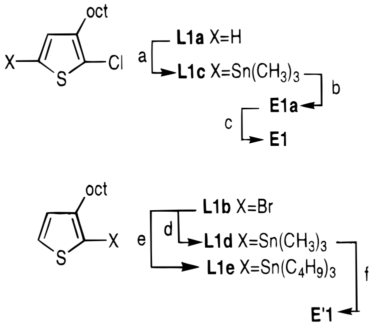
to the 3-octylthiophene) after 11 steps. The molecule **L6** was obtained in a quantitative yield after dehalogenation of **L6a** with tributyltin hydride (Scheme 7).

Study of the Coupling Reaction for Preparation of CG1 Series of Gels. The preparation of the CG1 gels series required to couple the B reactive functions of the cross-link M_2 (1,3,5 trisubstituted benzene) with the A reactive functions of the monomer $^1M_1$ (**L6**, see Scheme 2b). Two gelation thresholds were expected that corresponded respectively to an excess of monomers and of cross-links. The location of the gelation points were known to be directly related to the branching coefficient[19] α (probability for a cross-link to be connected to another one via **L6**). This coefficient α is a function of the average probabilities p_A and p_B for the functions A and B to react, ($p_A = rp_B$). The values of r corresponding to the two gelation thresholds (r_{c1} and r_{c2}) were roughly predicted within the mean field theory using the analogy between the sol–gel transition and the percolation model. The predicted values were $r_{c1} = 0.5/2p_A^2$ and $r_{c2} = 2p_B^2$: they were respectively equal to 0.5 and 2 if p_A or p_B were equal to 1 and became dramatically close one from another when p_A or p_B decreased. On one hand, the location of the gelation points at high r values was of interest because it allowed networks to get close to it with accuracy, but on the other hand, the distance between the two gelation points had to be large enough to allow gels of various structures related to various r values. Therefore, it was necessary to determine the experimental conditions that allowed p_A and p_B to be as high as possible. In other terms, the yield of the coupling reaction between $^1M_1$ and M_2 had to be as high as possible. That is the reason we had to choose a well-adapted coupling reaction and then to study the influence of the various experimental parameters on its yield.

First of all, we decided to rule out the Suzuki coupling for two reasons: (a) We observed during the preparation of **L6a** that the boronate function was not very stable; (b) before the emergence of the insoluble part (the gel) from the soluble part (the sol), the size of the finite clusters of the sol was known to increase dramatically. To obtain gels as homogeneous as possible, these finite clusters of great size had to be as well solvated as possible. Therefore, the reaction had to be performed at high temperature in an apolar solvent that was not compatible with the Suzuki reaction, which had to be carried out preferably in a mixture of water and organic solvent. The Stille coupling reaction[20] was chosen because the tin function was more stable than the boronate one and because it could be performed in an apolar solvent. Finally, the 1,3,5-tribromobenzene was chosen as M_2. The coupling reaction being chosen, we now had to optimize its yield. The three reactive functions B of M_2 were, at least at the beginning of the reaction, equivalent. It was not the case for the two reactive functions A of **L6** because the octyl chains induced a steric hindrance. In the literature,[21a] the steric hindrance was reported to be unfavorable to the Stille reaction because it induces an alkyl transfer from the tin derivative. Therefore, we decided to optimize the less favorable reaction (involving the Y position, Scheme 3) before testing the selected experimental conditions for the most favorable reaction (involving the X position). Because of their ease of synthesis, metalated derivatives of 3-*n*-octylthiophenes were chosen as model compounds. The tin derivative **L1c** was obtained from **L1a** in a quantitative yield by lithiation of the 5 position followed by quenching with trimethyltin chloride (Scheme 5). **L1b** was allowed to react with magnesium turnings, yielding the thienyl Grignard reagent, which was quenched with trimethyltin chloride or tributyltin chloride to give respectively the tin derivatives **L1d** or **L1e**. After purification, **L1d** and **L1e** were contaminated with approximately 7% of 3-*n*-octylthiophene [according to gas chromatography (GC)]. **L1d** and **L1e** were used without any further purification because the 3-*n*-octylthiophene was unreactive toward 1,3,5-tribromobenzene under Stille coupling reaction conditions.

Scheme 5. Study of Stille Coupling Reaction



(a) THF, BuLi, $(CH_3)_3SnCl$; (b) toluene, $Pd(PPh_3)_3$, reflux; (c) ethyl acetate, Pd/C, Triethylamine, H_2 50 Atm; (d) THF, Mg, $(CH_3)_3SnCl$; (e) THF, Mg, $(n\text{-}C_4H_9)_3SnCl$; (f) see Table 1 for the reaction conditions.

The reactivity of the two metalated 3-*n*-octylthiophenes toward 1,3,5-tribromobenzene was then studied. The results are summarized in Table 1. The course of all the coupling reactions was monitored by HPLC. First of all the tributyltin derivative **L1e** (less toxic than the trimethyltin derivative **L1d**) was allowed to react with tribromobenzene in the presence of the catalyst $Pd(PPh_3)_3$, which was used for the synthesis of **L6a** (Scheme 5 and Table 1, entry 1). The reaction stopped before completion: the intermediates **E′1.1** and **E′1.2** (Scheme 6) were detected in addition to the expected star molecule **E′1**. Moreover, the reaction gave a complex mixture of byproducts, which were not analyzed. The tin derivative **L1d** with methyl substituants was then allowed to react in the same conditions with tribromobenzene (Table 1, entry 2). After 65h, **E′1** was obtained in 60% yield without any trace of the intermediate compounds **E′1.1** and **E′1.2**. However, two impurities were detected and analyzed. The major one **E′1.2 g** (80% with respect to the second impurity according to HPLC) (Scheme 6) resulted from a transfer of the methyl instead of the thienyl during the transmetalation step of the Stille coupling reaction. This side reaction has already been described in the literature.[22]

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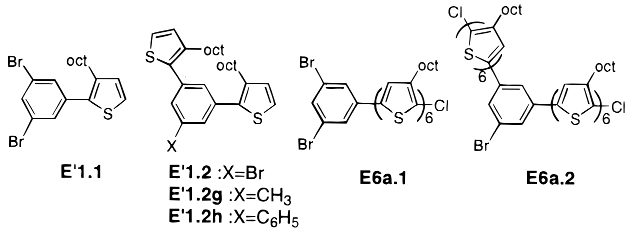
Table 1. Influence of Some Parameters on Yield of the Stille Coupling Reaction Yielding E′1

entry	tin derivative	catalyst	solvent	T	reaction time[a]	byproducts[b]	isolated yield
1	**L1e**	$Pd(PPh_3)_3$	toluene	110 °C	65 h	*c*	*d*
2	**L1d**	$Pd(PPh_3)_3$	toluene	110 °C	65 h	12%	60%
3	**L1d**	$Pd(PPh_3)_3$	*p*-xylene	120 °C	20 h	18%	53%
4	**L1d**	$Pd(PPh_3)_3$	*p*-xylene	134 °C	20 h	32%	40%
5	**L1d**	$Pd(PPh_3)_2Cl_2$	toluene	110 °C	24 h	6%	75%
6	**L1d**	$Pd(AsPh_3)_4$	toluene	110 °C	0.2 h	*c*	*d*
7	**L1d**	$Pd[P(2\text{-furyl})_3]_4$	toluene	110 °C	60 h	*c*	*d*
8	**L1d**	$Pd(PPh_3)_2Cl_2/CuI$	*p*-xylene	120 °C	1 h	10%	63%
9	**L1d**	$Pd(PPh_3)_2Cl_2$	DMF	120 °C	0.75 h	2%	84%
10	**L1d**	$Pd(PPh_3)_2Cl_2$	DMF/toluene (15/85)	118 °C	3 h	4%	78%
11	**L1d**	$Pd(PPh_3)_2Cl_2$	DMF/toluene (50/50)	126 °C	1 h	4%	78%
12	**L1d**	$Pd(PPh_3)_2Cl_2/CuI$	DMF	120 °C	0.02 h	5%	78%

[a] The reaction was considered complete when no more reaction occurred according to HPLC; long reaction times (>12 h) are overestimated. [b] Calculated with respect to **E′1** (according to HPLC). [c] Other byproducts were detected (see text). [d] Intermediates **E′1.1** or **E′1.2** were detected in a large amount and the reaction mixture was not purified.

Scheme 6. Intermediate Molecules and Byproducts: Description and Nomenclature



The second byproduct **E′1.2h** resulted from a phosphorus-to-palladium aryl transfer. This side reaction has likewise been reported.[23,24] However, the low yield could not only be explained by the formation of these two byproducts. Other minor byproducts were probably present but could not be separated by HPLC. Nevertheless we chose the trimethyltin derivative **L1d** because its reactivity toward tribromobenzene was higher than the reactivity of the tributyltin derivative **L1e**. Then our efforts were focused in increasing the yield in **E′1** and therefore in decreasing the yield of the main side reaction, the methyl transfer. First, the influence of the temperature was studied, while keeping the polarity of the solvent and the catalyst $Pd(PPh_3)_3$ constant. The entries 3 and 4 of Table 1 show that an increase of the temperature resulted in a lower yield for **E′1** and promoted the methyl transfer reaction. Nevertheless, decreasing the temperature below 110 °C should affect the homogeneity of the gels (see below). Therefore, temperatures of about 110 °C and 120 °C appeared realistic. The catalyst was the second parameter studied, the temperature (110 °C) and the solvent (toluene) being constant. The use of $Pd(PPh_3)_2Cl_2$ instead of $Pd(PPh_3)_3$ (Table 1, entry 5) resulted in an increase of the rate of the main reaction as expected and also in an increase of the yield. It had been observed[23] that the catalytic species was $Pd(PPh_3)_2$. In our case, this catalytic species should result from the reduction of 1 equiv of $Pd(PPh_3)_2Cl_2$ at the beginning of the reaction while homocoupling 2 equiv of the tin derivative **L1d**. Actually, this mechanism seemed to occur here because the product resulting from the homocoupling of **L1d** was detected in the expected amount. Other possible ligands for the palladium had been reported in the literature,[25] such as triphenyl arsine and tri-2-furyl phosphine. They were known to accelerate the reaction rate. We were interested in studying their effect on the methyl transfer in our experimental conditions. However, the catalyst $Pd(AsPPh_3)_4$ decomposed rapidly in refluxing toluene before the reaction was complete (Table 1, entry 6). In a same manner, the catalyst $[Pd(P(2\text{-furyl})_3)_4]$ decomposed before the end of the reaction after 60 h in refluxing toluene (Table 1, entry 7). In both cases new byproducts were detected in addition to **E′1.2 g** and **E′1.2h**. As a consequence, these two catalysts were not further studied and the catalyst $Pd(PPh_3)_2Cl_2$ was chosen. Then we studied the influence of a cocatalyst: copper (I) iodide. The role of this compound was still not completely understood[26] but it was reported to be efficient in avoiding the methyl transfer. The reaction was run in *p*-xylene (Table 1, entry 8). The catalyst decomposed just before the end of the reaction because traces of the intermediate **E′1.2** were detected. However a significant amount of the methyl transfer product **E′1.2 g** was detected. On the basis of these results, we decided to choose $Pd(PPh_3)_2Cl_2$ without any cocatalyst. Then we studied the influence of a third parameter: the solvent. Dimethylformamide (DMF) was considered despite its polarity because it often gives good results for Stille coupling reactions. DMF was used at high temperature (120 °C) to solvate the starting product **L6** used for the preparation of the gels. The reaction occurred rapidly and led to **E′1** in 84% yield (Table 1, entry 9). Other attempts conducted with mixtures of toluene and DMF gave moderate yields between the ones obtained with pure toluene or DMF (Table 1, entries 10 and 11). Finally, the use of copper iodide in DMF resulted in a small decrease in the yield of **E′1** (Table 1, entry 12). To summarize, the methyl transfer reaction is the main side reaction and is activated by the temperature; the use of other ligands than triphenylphosphine or cocatalysts as copper iodide did not

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(23) Farina, V.; Krishnamurthy, V.; Scott, W. J., Eds.; *The Stille Reaction*; John Wiley & Sons: 1997; Vol. 50, pp 2−641.

(24) (a) Segelstein, B. E.; Butler, T. W.; Chenard, B. L. *J. Org. Chem.* **1995**, *60*, 12−13. (b) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441−12453. (c) Morita, D. K.; Stille, J. K.; Norton, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 8576−8581.

(25) (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585−9595. (b) Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73−78. (c) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426−12435.

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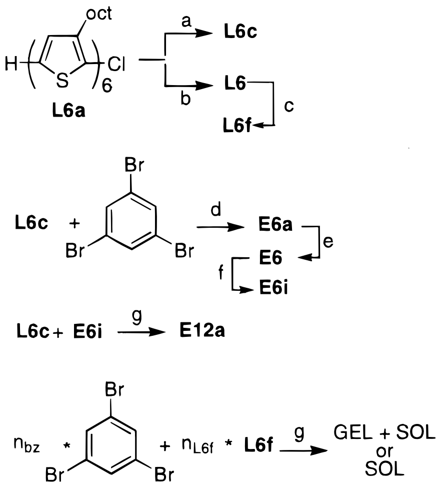
Scheme 7. Synthesis of Star Molecules E6a and E12a and the Series of Gels CG1



(a) THF, LDA, $(CH_3)_3SnCl$; (b) THF, Bu_3SnH, AIBN; reflux; (c) THF, BuLi, $(CH_3)_3SnCl$. (d) Toluene, $Pd(PPh_3)_3$, reflux; (e) ethyl acetate, Pd/C, triethylamine, H_2 60 atm, 65 °C; (f) chloroform/acetic acid 66/33 vol., I_2, $Hg(Oac)_2$; (g) toluene, $Pd(PPh_3)_2$, reflux.

allow us to circumvent this problem in the temperature and solvent conditions used. The best reaction conditions at high temperature, that is, the conditions that allow the decrease of the methyl transfer side reaction, are DMF as solvent and $Pd(PPh_3)_2Cl_2$ as catalyst. However, we chose toluene for the preparation of the gels because it seemed to us that it was the best compromise between the large cluster's solubility and the good yield of the reaction.

These conditions of reaction (indicated in Table 1, entry 5) selected from the study of the coupling in Y position (see Scheme 3), that is, from the study of the preparation of **E′1** from **L1d**, were tested for the coupling on the X position (see Scheme 3); they allowed us to obtain the star molecule **E1a** from **L1c** in 91% yield (Scheme 5). Consequently, they were chosen for the preparation of the gels. **E1a** could then be dechlorinated in a nearly quantitative yield to give **E1** using palladium on charcoal under a high-pressure hydrogen atmosphere (Scheme 5).

Synthesis of Star Molecules E6a and E12a (Respectively $^2M_1$ and $^3M_1$). *Synthesis of Star Molecule **E6a** (Scheme 7).* **L6c** was obtained in a quantitative way and a pure form after lithiation of the hexamer **L6a** and quenching with trimethyltin chloride. However, if butyllithium was used (as for the monomer **L1c**) a lithium−chlorine exchange was observed on **L6a**. This difference of reactivity between **L6a** and its monomer could be explained by a difference of charge density on the chlorine in **L6a** with respect to the one in **L1a** because of the delocalization along the oligomer. By analogy with this observation, a lithium−chlorine exchange had already been described for tetrachlorinated thiophenes.[27] Moreover, an oligomer size effect had already been reported for a protodesylilation reaction.[28] The lithium−chlorine exchange was completely circumvented using the less nucleophilic lithium diisopropyl amide (LDA). The star molecule **E6a** was then obtained in 80% yield by reacting 3.3 equiv of **L6c** with 1 equiv of 1,3,5-tribromobenzene. The intermediate molecules **E6a.1** and **E6a.2** were obtained after purification when using 1.5 eq. of **L6c**.

Table 2. CG1 Series of Gels: Initial Amount (mg) of (a) L6; (b) Tribromobenzene; (c) Initial Cross-Link Ratio *r* (as defined in the text); Amount of (d) Sol, (e) Gel at the End of the Reaction

L6f (mg) (a)	$C_6H_3Br_3$ (mg) (b)	*r* (c)	sol (mg) (d)	gel (mg) (e)
98.5	2.8	0.20	97	0
97.5	9.6	0.70	81	0
98.2	11	0.80	82	0
93.9	11.9	0.90	87.5	0
96.3	12.8	0.95	93.5	0
101.3	14.2	1.00	23	62
109.7	16.2	1.05	89	0
118	18.2	1.10	91	0
103.3	18.9	1.30	90	0
98.3	19.7	1.43	97	0
99.9	21.1	1.50	101	0
110.3	24.8	1.60	102	0
97.4	23.9	1.75	86	0
97.3	30.4	2.22	99	0

*Synthesis of Star Molecule **E12a** (Scheme 7).* **E6a** was dehalogenated using hydrogen and palladium on charcoal, thus leading to **E6** in a nearly quantitative way. **E6** was functionalized with iodine to give **E6i** in a nearly quantitative yield. **E12a** was obtained in 30% yield by coupling 3.15 equiv of **L6c** with 1 equiv of **E6i**.

Preparation of CG1 Series of Gels (Scheme 7). Bis-stanylated hexamer **L6f** was prepared quantitatively by treatment of **L6** with 2.2 equiv of butyllithium and then quenching with trimethyltin chloride. **L6f** was then allowed to react with 1,3,5-tribromobenzene in the conditions previously determined (Table 1, entry 5). However, in this case, the freshly prepared[29] Pd° catalyst $Pd(PPh_3)_2$ was used to avoid the homocoupling of **L6f**. The reaction was carried out without stirring to avoid damage to the gels, which were near the threshold. After 1 day of reaction, an additional amount of phosphine-free catalyst $Pd_2(dba)_3$ was added.[30] After 2 days of reaction, the toluene was removed and the residue was extracted with hot methanol to remove the remaining tin salts before a thorough extraction by chloroform using a Soxhlet apparatus. Experiments with different reticulation ratios *r* were performed ($0.20 \leq r \leq 2.22$, Table 2). The reticulation ratio *r* which was previously defined (eq 1), was equal in this case to:

$$r = (3 \times n_{\mathbf{bz}})/(2 \times n_{\mathbf{L6f}}) \quad (2)$$

where $n_{\mathbf{bz}}$ and $n_{\mathbf{L6f}}$ are respectively the amount (mole) of tribromobenzene (functionality $f = 3$) and of the hexamer **L6f** ($f = 2$). For $0.20 < r < 1.00$ on the one hand, and $1.00 < r < 2.22$ on the other hand, only a soluble phase (the sol) was isolated. For $r = 1.00$ an insoluble part (the gel) was also isolated with the soluble part. This result showed that the two r_c values r_{c1} and

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(27) Hill, B.; Vleeschauwer, M.; Belley, M. *Synlett.* **1998**, *4*, 407−410.

(28) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

(29) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1138−1139.

(30) After 1 day of heating, the initial catalyst Pd(PPh3)3was expected to be decomposed according to the observations from the monomers. An extra amount of catalyst was then added. The ligand-free catalyst Pd2(dba)3 was used rather than the initial catalyst because of the presence of the ligands resulting from the decomposition of the latter.

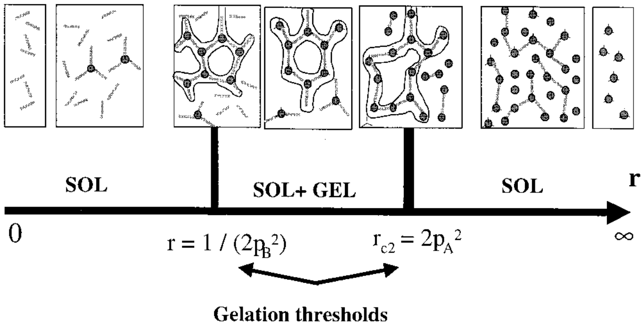

Figure 1. Schematic representation of the structure evolution of the systems GC1 as a function of *r*; ● filled circles represents the cross-link M$_2$ and connecting lines the monomer ^{1}M$_1$.

r_{c2} for which we observed gelation thresholds were respectively $0.95 < r_{c1} \leq 1.00$ and $1.00 < r_{c2} \leq 1.05$.

As explained in the introduction of this paper, two gelation thresholds were expected in these systems that were respectively related to an excess of the cross-links M$_2$ or of the monomers ^{1}M$_1$ (see Figure 1). Actually, we observed two gelation thresholds corresponding respectively to the cross-link ratios r_{c1} and r_{c2} that were very close one from another and approximately equal to 1. The cross-link ratio $r = 1$ corresponded to the case where, if p_a and p_b were equal to 1, each A reactive function could react with a B reactive function and vice versa: this cross-link ratio corresponded to the most cross-linked gel. We have shown in paragraph 2 of this chapter that the positions of the two gelation points were dependent on the yield of the coupling reaction between the tribromobenzene (cross-link) and the hexamer **L6f** (see also Figure 1). The case where $r_{c1} = r_{c2} = 1$ corresponded to $p_A = p_B = 0.7$ (p_A and p_B being respectively the probability for the functions A and B to react). With the two observed gelation thresholds corresponding to *r* values very close to 1, we could conclude that the effective p_A and p_B were very close to 0.7. That revealed that the effective average yield of the coupling reaction between the tribromobenzene (cross-link) and the hexamer **L6f** was lower than that predicted on model compounds. Fortunately, this effective yield was high enough to allow us to get one gel: the most cross-linked one. Only a very small decrease in this effective yield should have resulted in getting no gels, whereas only a small increase in the average effective yield of this coupling reaction should have resulted in a distance between r_{c1} and r_{c12} large enough to allow getting a large series of gels (for example $p_A = p_B = 0.8$ should lead to $r_{c1} = 0.78$ and $r_{c12} = 1.12$). The preparation of a large series of gels is necessary to study their statistical structure and to determine the variable suitable to predict any statistical state of gelation in these systems. Many physical quantities (the gel fraction, the swelling ratio, the conductivity in the swollen state)[11] should be a function of this relevant variable. Therefore the average yield of the coupling reaction has to be more increased and some modifications in the way of preparation will be proposed in the conclusion of this paper for that purpose. Nevertheless, we stress the fact that the 14 sols we have prepared (see Table 2) are very interesting, conducting branched systems, the properties of which will be reported in a next paper.

Characterization of Monomers ^{i}M$_1$ ($1 \leq i \leq 3$) and Intermediates. *^{1}H and ^{13}C NMR Spectroscopy.* The signals of the octyl chains proton and carbon atoms have already been assigned in the literature.[15,31]

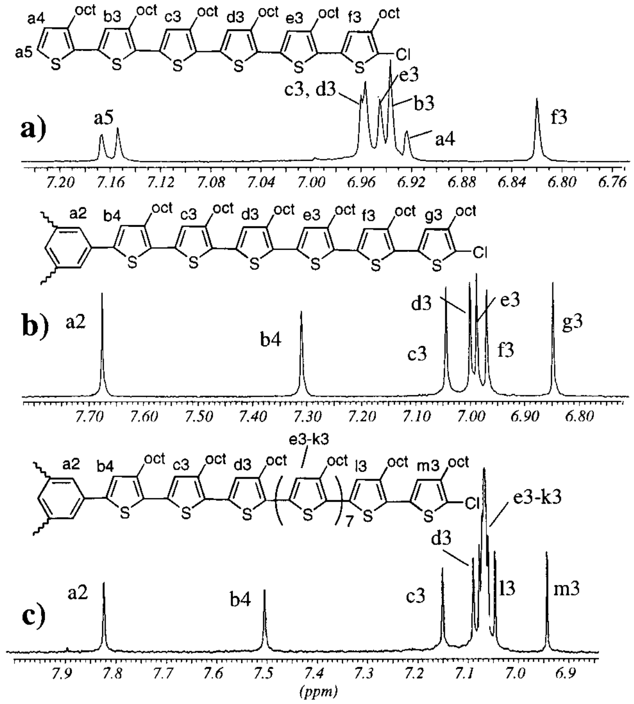

Figure 2. ^{1}H NMR spectra of the molecules (a) **L6a**, (b) **E6a**, and (c) **E12a** recorded respectively in CDCl$_3$, CD$_2$Cl$_2$, and THF-d8.

Concerning the aromatic region, the assignments of the ^{1}H signals of the molecule **L6** have already been described.[15] In the ^{1}H and ^{13}C NMR spectra of the tin-functionalized molecules (**L1c**, **L1d**, **L1e**, **L6c**, and **L6f**) we observed couplings between tin (^{117}Sn and ^{119}Sn) and respectively protons and carbons. The values of the coupling constants are reported in the experimental part.

The ^{1}H NMR spectra of the compounds **E1**, **E1a**, **E′1**, **E′1.1**, and **E′1.2** were in agreement with their structure. The signals of the ^{13}C NMR spectra of **E1**, **E1a** and **E′1** were assigned with two-dimensional NMR techniques (^{1}H-^{13}C HMBC and HMQC).

The signals of the ^{1}H spectrum (Figure 2b) of **E6a** were assigned on the basis of the assignments of **L6a** (Figure 2a) and mainly with a two-dimensional ^{1}H-^{1}H TROESY experiment (Figure 3). For a mixing time of 0.8s, the proton in a2 showed an intense dipolar interaction with the proton in b4. Increasing the mixing time to 1 s revealed an additional weak dipolar interaction between the protons of the benzene ring and the proton in c3. However, there was no dipolar interaction between the protons in b4 and in c3. This result suggested that the thiophene rings bearing the protons in b4 and in c3 were in an anti conformation. In this conformation the distance between the protons in b4 and in c3 [approximately 6 Å according to Corey-Pauling−Koltun (CPK) models] is too high to observe a dipolar correlation,[32] whereas the distance between the protons in c3 and in a6 (around 4 Å according to CPK models)

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[31] Ferrari, M.; Mucci, A.; Schenetti, L. *Magn. Reson. Chem.* **1995**, 33, 657−663.

[32] Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: 1996.

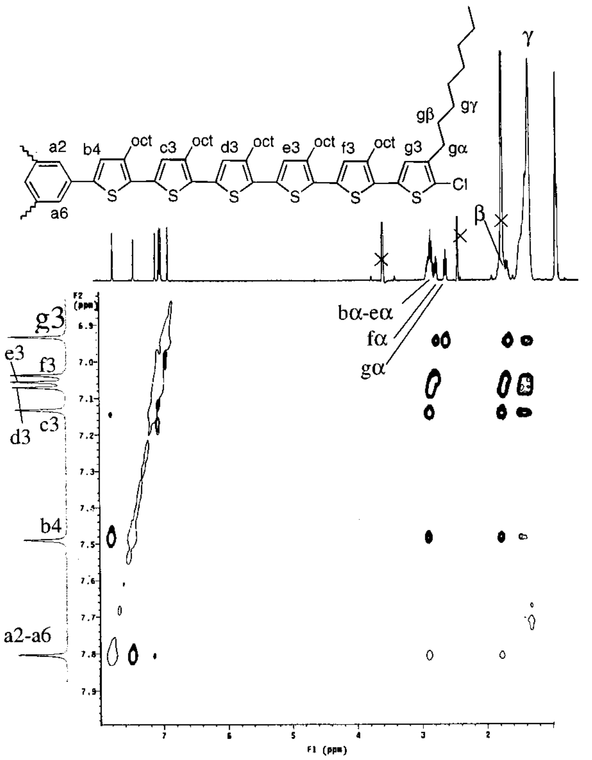
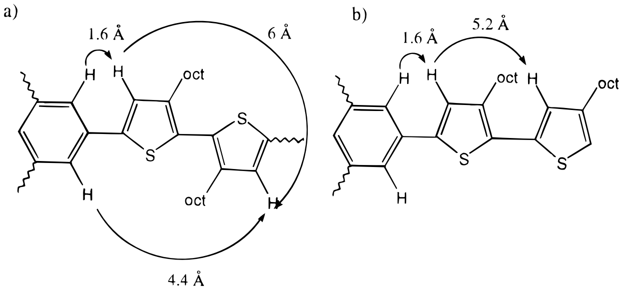


Figure 3. ^{1}H-^{1}H TROESY spectrum of **E6a** recorded in THF-d8 (mixing time of 1 s).

Scheme 8. Distances Measured on a CPK Model of E6A of the (a) Trans Configuration and (b) Cis Configuration



is low enough to observe a correlation (see Scheme 8). This was in agreement with the conformation of oligothiophenes usually reported in the literature.[33] Moreover, the observation of the dipolar interactions of the aromatic protons with the aliphatic protons (α, β, γ protons) allowed us to complete the assignment of the aromatic protons (Figure 3). The intermediates **E6a.1** and **E6a.2** were satisfactorily characterized by ^{1}H NMR. The ^{13}C assignment of **E6a** was performed using the assignment of **L6a** and **E1a** and two-dimensional ^{1}H-^{13}C HMQC and HMBC experiments.

The ^{1}H and ^{13}C assignments of the star molecule **E12a** (see Figure 2c for the ^{1}H spectrum) were performed according to the ^{1}H and ^{13}C assignments of **E6a.** The ^{1}H spectrum of **E12a** was preferentially carried out in tetrahydrofuran (THF)-D8 instead of $CDCl_3$ because the signals of the protons e3−k3 were better resolved.

Electronic Absorption Spectroscopy. The wavelengths (λ_{max}) related to the transitions of absorption of the linear oligomers ranging from **L2a** to **L6a** and to various star oligomers are presented in Table 3. The data reported in the literature for the linear chlorinated oligothiophenes[15] and for a regioregular HT polyoctylthiophene[34] are also presented in Table 3.

Table 3. Wavelength (λ_{max}) Related to Transitions of Electronic Absorption and Fluorescence in Chloroform of Linear Oligomers, of Star Oligomers, and of Polymer [Regioregular HT Poly(octylthiophene)]

compound	absorption λ_{max} (nm)	fluorescence λ_{max}(nm)
L2a	308[a]	437
L3a	344[a]	437, 454
L4a	372[a]	479, 502
L5a	393[a]	502, 532
L6a	405[a] (420[b])	527, 550
E1a	312	–
E1	300	–
E′1	280	–
E6a.1	418	–
E6a.2	420	–
E6a	422 (475[b])	550, 586
E12a	438 (515[b])	575, 618
polymer	453	577, 626

[a] Already reported in the literature.[15] [b] In the Solid State.

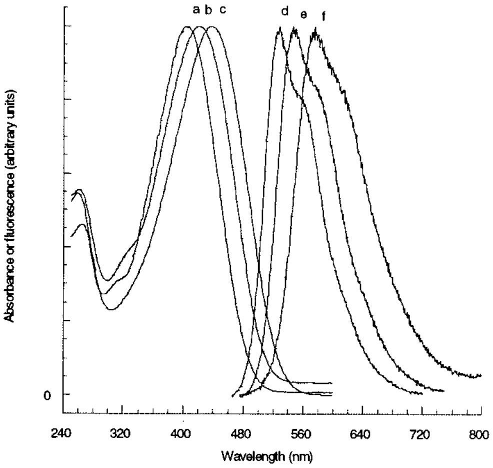


Figure 4. Absorbance and fluorescence spectra in chloroform of the compounds **L6a** (respectively a and d), **E6a** (respectively b and e), and **E12a** (respectively c and f).

The bathochromic shift (i.e., shift toward lower energies) of the absorption resulting in an increase in λ_{max} going from the 3-*n*-octylthiophene (240 nm) to the star molecule **E1a** (312 nm) was expected because of the presence of the benzene ring. The bathochromic shift for the compound **E1a** compared with **E1** could be explained by the auxochromic role (i.e., it induces a shift toward the lower energies) of the chlorine. The hypsochromic shift (i.e., shift toward higher energies) for the compound **E′1** compared with **E1** could be interpreted as the consequence of an increase of the dihedral angle between the thiophenes and the benzene because of the steric hindrance due to the octyl chains.

A strong bathochromic shift (i.e., increase in λ_{max}) in solution going from **L6a** to **E6a** was also observed and could be partly explained by the electronic delocalization on the benzene ring (see Figure 4). Nevertheless, an increase in λ_{max} from **E6a.1** to **E6a.2** and to the star molecule **E6a** was also observed. This result could be

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(33) DiCesare, N.; Belletete, M.; Marrano, C.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1998**, *102*, 5142−5149.

(34) Guillerez, S.; Bidan, G. *Synth. Met.* **1998**, 93, 123−126.

interpreted in terms of conjugation between different hexamer substituants via the benzene ring: this should be of great interest to correlate conductivity and topology in swollen gels. Nevertheless, no definitive conclusion could be drawn because both the influence of the bromine and of the sexioctylthiophene had also to be taken into account.

The λ_{max} corresponding to the transition of absorption of the compound **E12a** (see Figure 4) could not be directly compared with the λ_{max} of a related oligothiophene because no oligomer longer than the hexa(octylthiophene) had been synthesized. However, a linear relationst had been predicted between the energy (E_{max}) of the absorption transition and the reciprocal of the number of thiophenes n.[35] We already demonstrated for the regioregular HT oligo(3-octylthiophenes) **L2a**–**L6a** the following relation:[15]

$$E_{max} = 2.54 + 3.15/n \qquad (3)$$

We have shown that this linear relation was no more reliable for the related polymer ($n \rightarrow \infty$).[15] This was also true for other types of oligothiophenes.[36–41] As a consequence, it was not surprising that the value predicted with the eq 3 for a regioregular dodecaoctylthiophene (442 nm) was higher than the experimental value obtained for the star molecule **E12a** (438 nm), whereas the dodecaoctylthiophene was conjugated with the benzene ring in **E12a.** Nevertheless, this result allowed us to show that the upper limit of n for which eq 3 was valid was strictly less than 12.

The values of the maximum molar extinction coefficient (ϵ_{max}) of the star molecules **E6a** and **E12a** were consistent with the ϵ_{max} of the linear oligothiophene **L6a**. As a matter of fact, the ϵ_{max} of **E6a** (118 000 mol^{-1} cm^{-1}) and **E12a** (241 000 mol^{-1} cm^{-1}) were respectively approximately three times and six times as much as the ϵ_{max} of **L6a** (36 800 mol^{-1} cm^{-1}).

Contrary to the linear molecules **L2**–**L5** and the star molecules **E1** and **E′1**, the compounds **L6a**, **E6a**, and **E12a** exhibited good film-forming properties, and it was then possible to record their UV spectra in the solid state (Figure 5). Compared with the spectra in solution, their spectra in the solid state showed vibronic features. The bathochromic shift also observed (Table 3) revealed a more planar structure in the solid state than in solution.

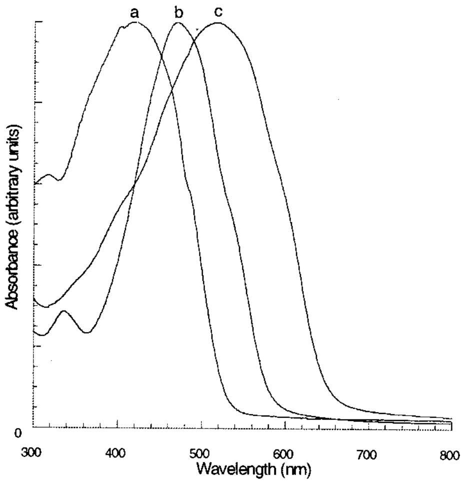

Figure 5. UV–vis absorption spectra of films cast from a chloroform solution of (a) **L6a**; (b) **E6a**; (c) **E12a**.

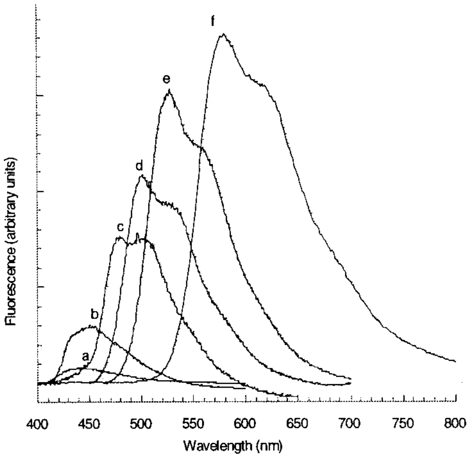

Figure 6. Fluorescence spectra recorded in chloroform of the oligomers (a) **L2a**; (b) **L3a**; (c) **L4a**; (d) **L5a**; (e) **L6a**, and (f) of the regioregular HT poly(3-*n*-octyl)thiophene. The scale of the spectra was chosen increasing with increasing the chain length for an easier reading.

Electronic Fluorescence Spectroscopy. The wavelengths (λ_{max}) related to the transitions of fluorescence of the linear oligomers **L2a** to **L6a**, of various star oligomers, and of the regioregular HT poly(octylthiophene) are reported in Table 3. The fluorescence spectra of the thiophene oligomers **L2a** to **L6a** and of the polymer in solution in chloroform are shown in Figure 6. All these compounds except the dimer **L2a** showed two distinct vibronic peaks separated by 0.10–0.17 eV and a shoulder at lower energy. The energy separation of the two vibronic peaks was consistent with a C=C stretching mode strongly coupled to the electronic structure.[42] The plot of the energy of the two distinct fluorescence peaks of the compounds **L3a**–**L6a** versus the reciprocal of the number n of thiophenes (Figure 7) could be linearly fitted by:

$$E_1 = 1.88 + 2.85/n \qquad (4)$$

$$E_2 = 1.77 + 2.85/n \qquad (5)$$

where E_1 and E_2 are respectively the energy (eV) of the

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[35] (a) Baughman, R. H.; Chance, R. R. *J. Polym. Sci. Polym. Phys. Ed.* **1976**, *14*, 2037–3045. (b) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

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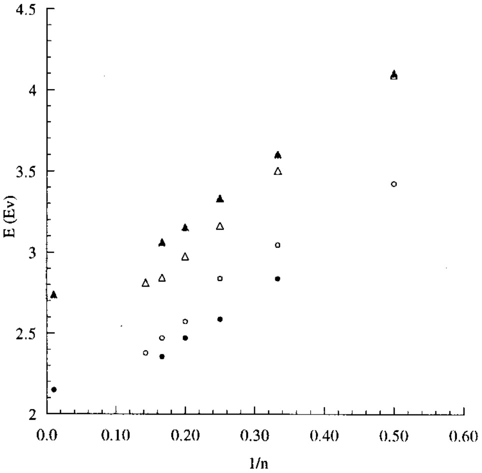

Figure 7. Energy of absorbance (▲ and △) and fluorescence (● and ○, highest energy band) versus the reciprocal number of thiophenes for the oligomers **L2a**–**L6a**, for the regioregular HT poly(3-*n*-octyl)thiophene (full filled symbols), and for the non substituted oligothiophenes (empty symbols).[38c]

peaks observed at lower (peak 1) and higher (peak 2) wavelength (see Figure 5). Such a linear correlation between the energy of the first and second bands of fluorescence has been reported for unsubstituted oligothiophenes.[38c] Equation 4 was more reliable because peak 1 was better resolved than peak 2. These equations did not take into account the α-chlorinated HT bithiophene **L2a** because its energy of luminescence did not fit the linear relations previously detailed. This was attributed to the auxochromic effect of the chlorine. It was in agreement with our previous results because **L2a** was the only chlorinated oligomer that exhibited a bathochromic shift in absorption compared with its nonchlorinated analogue **L2**. Concerning the HT polyoctylthiophene, the energy of its fluorescence transitions did not follow the linear eq 4 or 5. The fact that these linear relations were no longer valid for $n \to \infty$ could be explained in a same way as for absorption spectroscopy: long oligomers and the related polymer can be considered as semirigid chains where kinks delimit short oligomers that are responsible for the energies of absorption or fluorescence observed.[15]

The fluorescence spectra obtained for **E6a** and **E12a** (Figure 4) were of a shape similar to the ones of the linear oligo(octylthiophene)s. They showed the same resolved vibronic features and a bathochromic shift with respect to the absorption spectra. As expected from the absorption results, the fluorescence $\lambda_{\max}$ of the compound **E6a** was higher than that of the related oligomer **L6a**. If the wavelength of the fluorescence transition of the compound **E12a** (575 nm) was compared with the value predicted from eq 4 for a dodecaoctylthiophene (586 nm), it showed that the linear relation was no longer valid for $n = 12$ as reported for another type of oligothiophene.[43]

Difference in Electronic Absorption and Fluorescence Data. The Stock shift, which is taken as the magnitude of the difference between the wavelengths of the absorption and emission maxima,[44] revealed the expected change to a more planar state while dissipating energy during the lifetime of the excited state.[45] Comparing the absorption and fluorescence data of the oligo(octylthiophene)s and of their nonalkylated analogues (Figure 7),[38c] it was noteworthy that the difference between the energies of absorption and fluorescence transitions was higher for the alkylated oligomers. According to the literature,[46] this could be attributed to the double effect of the alkyl chains. On one hand, they allow the molecule to be better solvated: the molecule is then twisted and its conjugation lowered, resulting in a hypsochromic shift. On the other hand, the octyl chain has an inductive effect that induces a bathochromic effect. In the ground state, the two phenomena compete but the hypsochromic effect is preponderant. In the excited state, the backbone adopts a planar conformation and the bathochromic effect of the alkyl chains is the only effect observed.

The difference we observed between the structureless absorption spectra and the vibrationally resolved photoluminescence spectra was also attributed to the more planar rigid structure for the excited state.[47]

The Stock shift and the presence of vibronic features only in the fluorescence spectra of **E6a** and **E12a** led us to conclude that the two star molecules also exhibit a more rigid planar structure in the excited state.

To treat the chain length dependence of the optical absorption and fluorescence we also applied the linear eq 6[49] derived on the basis of the free electron gas model of Kuhn.[50] We used this treatment, which is commonly made for oligoenes, because it is generally accepted that the nature of the oligothiophenes is analogous to that of polyenes,[48] although oligothiophenes are different from oligoenes in that they are not alternate hydrocarbons because of contributions of sulfur orbitals to the π-electron system.

$$E = V_0 + \left(\frac{h^2}{4ml_0^{\,2}} - \frac{V_0}{4}\right)\frac{1}{N + 0.5} \qquad (6)$$

V_0 is the amplitude of the sinusoidal potential that corrects the free electron gas model for bond length alternation, N the number of conjugated double bonds, l_0 the length of the unit of conjugation (l_0 = one thiophene + one single bond), h the Planck constant, and m the mass of the electron. The energies of the optical transitions were plotted according to eq 6 as a function $1/N$+0.5. They were situated on a straight line. A linear fit gave

$$E_{\text{absorption}}\ (\text{eV}) = 2.45 + 7.43(1/N + 0.5) \text{ and}$$

$$E_{\text{fluorescence}}\ (\text{eV}) = 1.84 + 6.44(1/N + 0.5)$$

We only report the data of fluorescence corresponding to the best-resolved peak. The data related to the other less resolved peak should give the same results.

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The lower value of $V_{0\ \mathrm{fluorescence}}$ (1.84 eV) if compared with $V_{0\ \mathrm{absorption}}$ (2.45 eV) was in good agreement with a more planar rigid structure in the excited state (increase in the quinoid character[45,48]) than in the ground state. The slopes respectively equal to 7.43 and 6.44 yielded respectively the lengths of the conjugation unit l_{0G} and l_{0E} in the ground and excited state. The values of l_{0G} and l_{0E} were similar and approximately equal to 3.3 Å. They were in a fairly good agreement with the expected ones although they were obtained in a simplified way, that is using the molecular orbital theory in its free electron approximation corrected for bond alternation.

Conclusion

The kit of elementary units required to obtain three series of regioregular calibrated gels was prepared: the HT regioregular sexioctylthiophene (**L6**) and two star-shaped molecules made of a benzene ring meta trisubstituted by three **L6** or three regioregular (HT) segments **L6**−**L6** (respectively **E6a** and **E12a**). The ^{1}H and ^{13}C NMR assignments of the signals of the elementary units and intermediates were made: information concerning their conformation were obtained. Optical properties (UV−vis absorption and fluorescence) of linear and star oligomers were studied and compared. Concerning the fluorescence properties, a linear evolution of the energy of the fluorescence transitions of the linear regioregular oligooctylthiophene with the reverse of thiophene number was demonstrated for the first time. A leveling-off effect with oligooctylthiophene length was also observed by fluorescence for the first time to our knowledge.

We have obtained a first series of calibrated cross-linked systems by chemical condensation of 1,3,5-tribromobenzene and regioregular HT sexioctylthiophene. They are related to cross-link ratios *r* ranging between 0.20 and 2.22. Two high gelation thresholds were observed. They respectively corresponded to two cross-link ratios $0.95 < r_{c1} < 1.00$ and $1.00 < r_{c2} < 1.05$. The two cross-link ratios r_{c1} and r_{c2} were very close one from another. Gelation thresholds related to such high *r* values presented the advantage allowing the preparation of systems close to the gelation thresholds with accuracy. Nevertheless, the short distance between the two thresholds needed to be increased to obtain a larger series of gels. Therefore the yield of the coupling reaction has to be still more increased. One solution may be to add an unsubstituted thiophene in position Y of the oligomer **L6** (Scheme 3) to avoid the steric hindrance due to the octyl chain. This method can also be recommended for the series CG2 and CG3. Nevertheless, we stress the fact that the various sols we have obtained are very interesting for two reasons: First, their structure, easy to study because of their solubility, is closely related to that of the gels; second, these sols are conducting branched polymers, which present an intrinsic potential interest.

Experimental Section

Reagents. All the chemicals were purchased from Aldrich Chemical Co. except the 3-*n*-octylthiophene, which was purchased from LCSO/ESCIL, Université Lyon 1, F-69622 Villeurbanne Cedex.

General Aspects. All manipulations were carried out under a dry oxygen-free argon atmosphere. Trialkyltin chloride and diisopropylamine were weighted and charged in reaction flasks in an argon drybox. Dry THF was distilled under argon from sodium benzophenone ketyl immediately before use. Dry toluene was distilled under argon from calcium chloride. Dry DMF was distilled under reduced pressure from molecular sieves. The solvents were then kept on molecular sieves. HPLC experiments were conducted on a Waters Delta Prep 4000 chromatograph equipped with an absorbance detector tuned at 254 or 400 nm. A Varian 2010 pump was used for the analytical Nucleosil column. Analyses were performed using two cartridges (Nova-Pak C18, 6 μm, 60 Å, 8 × 100 mm) or a Nucleosil column (10 μm, 250 × 4.6 mm). Preparative runs were performed using three PrepPak cartridges (Delta-Pak C18, 15 μm, 100 Å, 40 × 100 mm) or a Nucleosil column (10 μm, 250 × 21 mm). Column chromatography was performed using Silica (60 Å, 70−200 μm, 5500 $m^2\ g^{-1}$) purchased from SDS. Capillary GC analyses were obtained using a Varian Vista 6000 gas chromatograph equipped with a Chrompack capillary column (Cpsil5CB, 25 m × 0.32 mm, df = 0.11 μm) and a FID detector. Melting points were measured an Olympus BH2 microscope equipped with a Mettler FP82 hot stage. One-dimensional proton and carbon NMR spectra were recorded on a Brücker AC-200 spectrometer (operating at 200 MHz for the proton and 50 MHz for the carbon) or on an AM-400 spectrometer (operating at 400 MHz for the proton and 100 MHz for the carbon). Two-dimensional spectra were recorded on a Varian U400 spectrometer operating at 400 MHz for the proton and 100 MHz for the carbon. The solvents were purchased from Eurisotop and used as internal references. Chemical shifts (δ) were reported in parts per million (ppm) downfield from trimethylsilane and referred to the solvent (for protons: 7.26 ppm for $CHCl_3$, 5.32 ppm for CH_2Cl_2, 3.57 and 1.82 ppm for THF; for carbons: 77.7 ppm for $CDCl_3$ and 53.7 ppm for CD_2Cl_2). The coupling constants only deal with protons unless specified (s = singlet, d = doublet, dd = doublet of doublet, t = triplet). The coupling constants with two isotopes of tin (^{117}Sn and ^{119}Sn) are detailed unless they could not be resolved. The positions of the aromatic hydrogen or carbon atoms were numbered according to the Figures 1 and 2. Positive fast atom bombardment (FAB+) was performed on a VG analytical ZAB−SEQ or a VG masslab TRIO 2 mass spectrometer using *m*-nitrobenzyl alcohol as matrix. Electrospray spectra were performed on a LCQ quadrupole ion trap (Thermoquest) spectrometer using chloroform as solvent. MALDI-TOF spectra were recorded on a Voyager Elite X, Perspective Biosystems using 2,5-dihydroxybenzoic acid as the matrix. Elemental analyses were carried out by the Service Central d'Analyses, CNRS, B. P. 22, 69390 Vernaison, France. UV spectra were recorded on a Perkin-Elmer Lambda 9000 spectrometer using 1-mm path cells and low-concentration solutions ($10^{-4}-10^{-5}$ mol L^{-1}). Luminescence spectra were recorded using a mercury lamp (365 nm), a H20 Jobin-Yvon monochromator, and GaAs photomultiple. The concentration of the solutions used was $10^{-5}-10^{-6}$ mol l^{-1}.

Preparation of the Linear Monomers and Oligomers. *2-Chloro-3-octyl-5-trimethyltin Thiophene (**L1c**).* A solution of **L1a** (1.51 g, 6.33 mmol) in 20 mL of dry THF was cooled to −80 °C. Butyllithium, 2M (3.5 mL, 7 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then cooled to −80 °C before its transfer via cannula on trimethyltin chloride (1.38 g, 6.95 mmol) cooled at −80 °C. The reaction mixture was allowed to warm to room temperature. The reaction, monitored by GC, was pursued for 30 min and then poured in 200 mL of hexane. The solution was thoroughly washed with water and brine. After drying over sodium sulfate, the solvents were evaporated to give 2.36 g (93%) of a slightly brown oil, purity (GC) > 98%; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm) 6.88 (s, 0.8H; d, 0.2H, $^{3}J_{Sn-H}$ = 28.3 Hz; H4), 2.55 (m, 2H), 1.56 (m, 2H), 1.26 (m, 10H), 0.87 (m, 3H), 0.33 (s, 7.2H), 0.33 (d, $^{2}J_{117Sn-H}$ = 55.6 Hz, 0.9H), 0.33 (d, $^{2}J_{119Sn-H}$ = 58.1 Hz, 0.9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 141 (C3), 136.7 (C4), 136,7 (C3, d, $^{2}J_{Sn-C}$ = 24.3 Hz), 135.4 (C5), 129.9 (C2), 32.6, 30.5, 30.1, 29.9, 28.6, 23.4, 14.8,

−8.7 (s; d, $^{1}J_{\mathrm{Sn-C}} = 360$ Hz); MS (FAB) 378.9 (M-15), calc. for $C_{15}H_{27}ClSSn$: 394.

*2-Trimethyltin-3-octyl Thiophene (**L1d**).* To magnesium turnings (0.205 g, 8.45 mmol) in anhydrous THF (25 mL) heated to maintain a mild reflux was added dropwise **L1b** (1.5 g, 5.45 mmol). At the end of the addition, the reaction mixture was refluxed for 1 h and then transferred via cannula on trimethyltin chloride at room temperature (1.68 g, 8.45 mmol). The solution was poured in 200 mL of hexane, washed with water and brine, and dried over sodium sulfate. The solvents were evaporated to produce 1.71 g (81%) of a brown oil, purity (GC) > 93%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.52 (d, $^{3}J = 4.6$ Hz, 0.8H; dd, $^{3}J = 4.6$ Hz, $^{4}J_{\mathrm{Sn-H}} = 13.7$ Hz, 0.2H; H5), 7.09 (d, $^{3}J = 4.6$ Hz, 0.8H; dd, $^{3}J = 4.6$ Hz, $^{4}J_{\mathrm{Sn-H}} = 8.3$ Hz, 0.2H; H4), 2.62 (m, 2H), 1.58 (m, 2H), 1.28 (m, 10H), 0.88 (m, 3H), 0.37 (s, 7.2H), 0.37 (d, $^{2}J_{\mathrm{119Sn-H}} = 57.0$ Hz, 0.9H; d, $^{2}J_{\mathrm{117Sn-H}} = 54.5$ Hz, 0.9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 151.5 (C3), 131.9 (C2), 131.2 (s; d, $^{4}J_{\mathrm{Sn-C}} = 21.2$ Hz; C5), 130.0 (s; d, $^{3}J_{\mathrm{Sn-C}} = 40.9$ Hz; C4), 33.4, 33.3, 33.1, 32.9, 32.6, 31.0, 30.4, 30.3, 30.0, 23.4, 14.8, 9.5, −6 (s; d, $^{1}J_{\mathrm{Sn-C}} = 360$ Hz).

*2-Tributyltin-3-octyl Thiophene (**L1e**).* To magnesium turnings (0.274 g, 11.3 mmol) in anhydrous THF (25 mL) heated to maintain a mild reflux was added dropwise **L1b** (2.0 g, 7.27 mmol). At the end of the addition, the reaction mixture was refluxed for 1 h and then transferred via cannula on tributyltin chloride (2.25 g, 11.3 mmol). The solution was poured in 200 mL of hexane, washed with water and brine, and dried over sodium sulfate. The crude product was purified by preparative HPLC (Delta-Pak columns) using dichloromethane:acetonitrile mixtures (30:70) as eluents. The solvents were evaporated to produce 3.5 g (79%) of a brown oil, purity (HPLC) > 99%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.53 (d, $^{3}J = 4.8$ Hz, 0.8H; dd, $^{3}J = 4.6$ Hz, $^{4}J_{\mathrm{Sn-H}} = 11$ Hz, 0.2H; H5), 7.10 (d, $^{3}J = 4.5$ Hz, 0.8H; dd, $^{3}J = 4.5$ Hz, $^{4}J_{\mathrm{Sn-H}} = 8$ Hz, 0.2H; H4), 2.9 (m, 2H), 1.7−0.8 (m, 42H).

*3,4′,4″,4‴,4⁗,4′′′′′-Sexioctyl-5-trimethyltin-5′′′′′-chloro-2,2′:5′,2″:5″-2‴:5‴-2⁗:5⁗-2′′′′′-sexithiophene (**L6c**).* A solution of LDA was prepared before the reaction as follows: 4.5 mL (7.17 mmol) of butyllithium were added dropwise at room temperature to a solution of diisopropylamine (1.1 mL, 7.9 mmol) in 15 mL of THF. The solution was stirred at −40 °C for 40 min.

A solution of **L6a** (500 mg, 0.416 mmol) in 20 mL of dry THF was cooled to 0 °C. The LDA [1.21 mL (0.458 mmol)] solution previously prepared was added dropwise. The resulting solution turned orange to dark red. The solution was warmed to room temperature. One milliliter (0.502 mmol) of a solution of trimethyltin chloride in dry THF was added. After 1 h, the reaction mixture was poured in 200 mL of hexane. The solution was washed with 200 mL of ammonium chlorine and brine and dried on sodium sulfate. The solvents were evaporated, providing 565 mg (99%) of a red solid, purity (^{1}H NMR) > 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 6.99 (s, 0.8H; d, $^{3}J_{\mathrm{Sn-H}} = 27.2$ Hz, 0.2H, H4a), 6.955 and 6.95 (s and s, 1H and 1H, H3c or H3d), 6.94 (s, 1H, H3e), 6.93 (s, 1H, H3b), 6.82 (s, 1H, H3f), 2.73 (m, 8H), 2.71 (m, 2H), 2.57 (m, 2H), 1.68 (m, 12H), 1.28 (m, 60H), 0.88 (m, 18H), 0.38 (s, 7.2H; d, $^{2}J_{\mathrm{119Sn-H}} = 57.6$ Hz, 0.9H), 0.37 (d, $^{2}J_{\mathrm{117Sn-H}} = 54.5$ Hz, 0.9H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 141.4, 140.8, 140.6, 140.6, 140.5, 140.4, 139.1, 137.1, 136.9, 135.1, 134.7, 134.7, 134.6, 132.9, 130.9, 130.9, 130.8, 130.5, 129.2, 129.1, 129.1, 127.0, 124.8, 32.6, 31.5, 31.3, 31.2, 31.2, 30.4, 30.3, 30.3, 30.2, 30.1, 30.1, 30.0, 29.9, 28.7, 23.4, 14.8, −5.4; MS (ES) 1365 (M+1), calc. for $C_{42}H_{60}S_3$: 1364.

*3,4′,4″,4‴,4⁗,4′′′′′-Sexioctyl-2,2′:5′,2″:5″-2‴:5‴-2⁗:5⁗-2′′′′′-sexithiophene (**L6**).* A solution of **L6a** (512 mg, 0.425 mmol), a few milligrams of AIBN and tributyltin hydride (457 Fl, 1.7 mmol) in 5 mL of dry THF was refluxed for 10 h. A large excess of *p*-toluene sulfonic acid was added to hydrolyze the byproduct resulting from the chlorine−tributyltin exchange. After 1 h, the reaction mixture was poured in 200 mL of hexane. The solution was thoroughly washed with water and brine and dried over sodium sulfate. The solvents were evaporated and the crude product was purified with HPLC to remove the tin salts and provided 474 mg (95%) of an orange solid, purity (HPLC) > 99%.

*3,4′,4″,4‴,4⁗,4′′′′′-Sexioctyl-5,5′′′′′-bistrimethyltin-2,2′:5′,2″:5″-2‴:5‴-2⁗:5⁗-2′′′′′-sexithiophene (**L6f**).* To a red solution of **L6** (494 mg, 0.423 mmol) in 20 mL of dry THF cooled at −80 °C, butyllithium (513 μL, 1.057 mmol) was added dropwise. The solution turned from red to dark red. The solution was allowed to warm to room temperature and then immediately cooled to −80 °C. A solution of trimethyltin chloride in THF [0.91 mL (1.06 mmol)] was added dropwise. At the end of the addition, the solution was warmed to room temperature. The color turned to orange. After 30 min, the reaction mixture was poured in 200 mL of hexane. The solution was thoroughly washed with water and brine and dried over sodium sulfate. The solvents were evaporated, providing 625 mg (99%) of a thick orange oil, purity (HPLC) > 99%; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm) 7.15 (s, 0.8H; d, $^{4}J_{\mathrm{Sn-H}} = 7.5$ Hz, 0.2 H, H3f), 7.04 (s, 0.8H, H4a), 7.04 (d, $^{3}J = 26.9$ Hz, 0.2H, H4a), 7.01 [m, 3H, H3(c−e)], 6.97 (s, 1H, H3b), 2.79 (m, 10H), 2.62 (m, 2H), 1.68 (m, 12H), 1.31 (m, 60H), 0.90 (m, 18H), 0.40 (s, 7.2H; d, $^{2}J_{\mathrm{117Sn-H}} = 55.6$ Hz, 0.9H; d, $^{2}J_{\mathrm{119Sn-H}} = 58.1$ Hz, 0.9H), 0.37 (s, 7.2H; d, $^{2}J_{\mathrm{117Sn-H}} = 55.6$ Hz, 0.9H; d, $^{2}J_{\mathrm{119Sn-H}} = 58.1$ Hz, 0.9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 141.3, 140.4, 140.3, 139.8, 139.0, 137.0, 136.5, 134.9, 134.3, 134.0, 133.7, 133.0, 131.7, 131.05, 130.8, 130.5, 129.0, 128.7, 128.6, 33.3, 32.6, 31.3, 29.3, 29.5, 29.8, 23.3, 14.5, −7.7, −8.1; MS (FAB) 1493 (M+1), calc. for $C_{78}H_{126}S_6Sn_2$: 1492.

Preparation of Star Molecules, Intermediates, and Side Reaction Products. *1,3,5-Tris(3-octylthiophene-2-yl)-benzene (**E′1**).* A solution of **L1d** (0.340 g, 0.835 mmol) or **L1e** (0.407 g, 0.797 mmol) and 1,3,5-tribromobenzene (79.7 mg, 0.253 mmol) in 20 mL of dry solvent was carefully degassed. In some experiments, copper (+I) iodide (3 mg, 0.0157 mmol) was added. Catalyst 0.09 equiv was added before the reaction was allowed to warm to the desired temperature. At the end of the reaction, the toluene was evaporated and the crude product filtered on silica gel using hexane as eluent. The solvent was removed and the crude product was purified by preparative HPLC (Delta-Pak columns) using dichloromethane: acetonitrile mixtures (35:65) as eluents providing a colorless oil, purity (HPLC) > 99%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.46 (s, 3H, Ha2), 7.26 (d, $^{3}J = 5.1$ Hz, 3H, Hb2), 7.00 (d, $^{3}J = 5.1$ Hz, 3H, Hb3), 2.73 (m, 6H), 1.64 (m, 6H), 1.25 (m, 30H), 0.85 (m, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 139.7 (Cb4), 137.8 (Cb5), 136.0 (Ca1), 130.2 (Cb3), 129.6 (Ca2), 124,6 (Cb2), 32.6, 31.8, 30.45, 30.3, 30.2, 30.0, 29.6, 23.4, 14.8; MS (FAB) 660.1 (M^{C+}), calc. for $C_{42}H_{60}S_3$: 660.4. Anal. (calcd): C, 76.43 (76.30); H, 9.45 (9.15); S, 13.70 (14.55).

*1,3,5-Tris(2-chloro-3-octylthiophene-5-yl)benzene (**E1a**).* A solution of **L1c** (1.27 g, 3.12 mmol) and 1,3,5-tribromobenzene (0.312 g, 0.992 mmol) in 45 mL of dry toluene was carefully degassed. One milliliter of a solution (0.03 mmol mL^{-1}) of $Pd(PPh_3)_3$ was added and the reaction mixture was allowed to reflux for 3 h. The toluene was then evaporated and the crude product filtered on silica gel using hexane as eluent. The solvent was removed and the crude product was purified by preparative HPLC (Delta-Pak columns) using a dichloromethane:acetonitrile mixture (80:20) as eluent, providing 0.689 g (91%) of a slightly yellow solid, purity (HPLC) > 99%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.48 (s, 3H, Ha2), 7.08 (s, 3H, Hb4), 2.60 (m, 6H), 1.63 (m, 6H), 1.28 (m, 30H), 0.89 (m, 9H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 141.2 and 139.9 (Cb3 or Cb5), 135.9 (Ca1), 125.2 (Cb2), 125.1 (Cb4), 122.1 (Ca2), 32.6, 30.4, 30.1, 30.0, 28.9, 23.4, 14.8; MS (FAB) 765.1 (M+1), calc. for $C_{42}H_{57}Cl_3S_3$: 764.3. Anal. (calcd): C, 66.5 (65.99); H, 7.61 (7.52); Cl, 13.36 (13.91); S, 12.21 (12.58).

*1,3,5-Tris(3-octylthiophene-5-yl)benzene (**E1**).* A mixture of **E1a** (0.367 g, 0.48 mmol), 10% palladium on charcoal (0.255 g, 0.240 mmol) and triethylamine (1 mL, 7.17 mmol) in 150 mL of ethyl acetate was stirred for 24 h under 50 atm of hydrogen. The reaction mixture was filtered on Celite and washed with 200 mL of a 10% solution of hydrochloric acid, brine, and a saturated solution of sodium carbonate. The crude product was purified by preparative HPLC (Delta-Pak columns) using a dichloromethane:acetonitrile mixture (50:50) as eluent, providing 0.254 g (80%) of a colorless oil, purity (HPLC) > 99%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.67 (s, 3H, Ha2), 7.24 (d, $^4J = 1.5$ Hz, 3H, Hb4), 6.91 (d, $^4J = 1.5$ Hz, 3H, Hb2), 2.73 (m, 6H), 1.64 (m, 6H), 1.25 (m, 30H), 0.85 (m, 9H); ^{13}C NMR (CD_2Cl_2, 50 MHz) δ (ppm) 144.9 and 143.3 (Cb3 and Cb5), 136.2 (Ca1), 125.6 (Cb4), 122.2 (Ca2), 120.4 (Cb2), 32.3, 31.0, 30.9, 29.9, 29.8, 29.7, 23.1, 14.3; MS (FAB) 661.5 (M+1), calc. for $C_{42}H_{60}S_3$: 660.4. Anal. (calcd): C, 76.39 (76.30); H, 9.26 (9.15); S, 14.76 (14.55).

*Star Molecule (**E6a**).* A solution of **L6c** (560 mg, 0.377 mmol) and 1,3,5-tribromobenzene (37.7 mg, 0.120 mmol) in 30 mL of dry toluene was carefully degassed. The catalyst $Pd(PPh_3)_3$ (0.06 equiv) was added. After 12 h of stirring under reflux, the solvent was evaporated and the crude product was purified either by column chromatography using silica gel and a mixture of chloroform:hexane (8:92) as eluent or by preparative HPLC (Nucleosil columns) using a mixture of dichloromethane: hexanes (8:92) as eluent. A red solid [353 mg (80%)] was isolated, purity (HPLC) > 99%. Mp: 68 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm) 7.68 (s, 3H, Ha2), 7.31 (s, 3H, Hb4), 7.04 (s, 3H, Hc3), 7.00 (s, 3H, Hd3), 6.99 (s, 3H, He3), 6.97 (s, 3H, Hf3), 6.85 (Hg3), 2.77 (m, 24H), 2.71 (m, 6H), 2.57 (m, 6H), 1.69 (m, 36H), 1.29 (m, 180H), 0.89 (m, 54H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 141.4−141.2 (Ca1−Cb3), 140.8−140.6−140.55−140.5−140.4 [C(c−g)4], 136.0 (Cb5), 134.7−134.6−134.5−134.4 [C(c−f)2], 132.95 (Cg2), 131.5 (Cb2), 131.2−131.1−131.0 [C(c−e)5], 130.5 (Cf5), 129.3 (Cc2), 129.2−129.2 (Cd3 and Ce3), 129.0 (Cf3), 127.6 (Cb4), 127.0 (Cg3), 124.8 (Cg5), 122.1 (Ca2), 32.6, 32.4, 31.4, 31.3, 31.2, 30.4, 30.3, 30.3, 30.2, 30.2, 30.1, 30.1, 30.0, 30.0, 30.0, 29.6, 28.7, 23.4, 23.2, 14.8; MS (MALDI-TOF) 3678.6, calc. for $C_{222}H_{327}S_{18}Cl_3$: 3679.0; Anal. (calcd): C, 72.31 (72.47); H, 8.96 (8.96); Cl, 2.82 (2.89); S, 15.22 (15.69).

*Star Molecule (**E6**).* A mixture of **E6a** (200 mg, 0.054 mmol), palladium on charcoal 10% weight (160 mg, 0.150 mmol), and triethylamine (2 mL, 14.3 mmol) in 150 mL of ethyl acetate was stirred for 5 days at 65 °C under 60 atm of hydrogen. The reaction mixture was filtered on Celite and washed with 200 mL of a 10% solution of hydrochloric acid, brine, and a saturated solution of sodium carbonate. The solvents were evaporated and 187 mg (96%) of a red solid were obtained, purity (^{1}H NMR) > 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.68 (s, 3H, Ha2), 7.27 (s, 3H, Hb4), 7.04 (s, 3H, Hc3), 6.99−6.98−6.97 [s, 12H, H(d−g)3], 6.90 (d, $^4J = 1.5$ Hz, 3H, Hg5), 2.76 (m, 30H), 2.62 (m, 6H), 1.69 (m, 36H), 1.29 (m, 180H), 0.89 (m, 54H); MS (MALDI-TOF) 3577, calc. for $C_{222}H_{327}S_{18}Cl_3$: 3573.0.

*Star Molecule (**E6i**).* A solution of **E6** (187 mg, 0.052 mmol) in a mixture of chloroform: acetic acid (66:33) was vigorously stirred. Mercuric acetate (30.2 mg, 0.095 mmol) was added. After 10 min, iodine (43.8 mg, 0.172 mmol) was added. After 5 h, the reaction mixture was poured in 200 mL of hexane. The solution was washed with water, sodium bicarbonate, aqueous sodium thiosulfate, and brine and dried over sodium sulfate. A red solid [210 mg (99%)] was obtained, purity (^{1}H NMR) > 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.68 (s, 3H, Ha2), 7.27 (s, 3H, Hb4), 7.04 (s, 3H, Hc3), 6.99−6.97−6.95 [s, 9H, H(d−f)3], 6.78 (s, 3H, Hg3); MS (MALDI-TOF) 3956, calc. for $C_{222}H_{327}S_{18}I_3$: 3951.

*Star Molecule (**E12a**).* A solution of **E6i** (210 mg, 0.053 mmol) and **L6c** (240.5 mg, 0.176 mmol) in 25 mL of dry toluene was degassed. $Pd(PPh_3)_2$ (0.09 equiv) was added. After 12 h of reflux, the solvent was evaporated and the crude product was filtered on silica gel using a mixture of dichloromethane: hexane (10:90) as eluent. A purification by preparative HPLC using the Nucleosil columns and a mixture of dichloromethane: hexane (10:90) as eluent afforded 115 mg (30%) of a purple solid, purity (HPLC) > 99%. Mp: 120 °C; ^{1}H NMR (THF-D8, 400 MHz) δ (ppm) 7.81 (s, 3H, Ha2), 7.50 (s, 3H,Hb4), 7.15 (s, 3H, Hc4), 7.09 (s, 3H, Hd4), 7.07 [m, 21H, H(e−k)3], 7.05 (s, 3H, Hl3), 6.95 (s, 3H, Hm3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 141.4−141.3 (Ca1−Cb3), 140.8−140.6−140.4 [C(c−m)4], 136.1 (Cb5), 134.7−134.4 [C(b−l)2], 132.9 (Cm2), 131.5 (Cb2), 131.3−131.2−131.0 (C(c−k)2), 130.6 (Cl5), 129.5 (Cc3), 129.3 [C(d−k)3], 129.1 (Cl3), 127.7 (Cb4), 127.0 (Cm3), 124.8 (Cm5), 122.3 (Ca2), 32.8, 32.6, 32.6, 32.4, 32.1, 31.6, 31.4, 31.3, 31.2, 30.9, 30.4, 30.35, 30.3, 30.2, 30.15, 30.1, 30.05, 30.0, 29.95, 29.9, 27.7, 23.5, 23.4, 23.2, 14.95, 14.8; MS (MALDI-TOF) 7175, calc. for $C_{438}H_{651}S_{36}Cl_3$: 7177; Anal. (calcd): C, 72.38 (73.29); H, 9.19 (9.14); Cl, 1.74 (1.48); S, 15.20 (16.08).

Preparation of Gels. A solution of **L6f** and 1,3,5 tribromobenzene in 15 mL of toluene was carefully degassed. $Pd(PPh_3)_2$ (0.09 equiv) was added. The reaction mixture was allowed to reflux for 1 day without stirring. Then 0.045 equiv of $Pd_2(dba)_3$−chloroform adduct in solution in degassed THF were added. After another day of refluxing, the solvent was evaporated and the crude product was washed with hot methanol before being extracted in a Soxhlet apparatus with chloroform for 3 days. The chloroform was evaporated to lead to a red solid (the sol), and a red solid was recovered in the cartridge (the gel).

Intermediate Molecules and Byproducts. *Homocoupling Product (3,3′-Dioctyl-2,2′-bithiophene).* This product was isolated from the purification of **E′1**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.28 (d, $^3J = 5.1$ Hz, 2H), 6.96 (d, $^3J = 5.1$ Hz, 2H), 2.49 (m, 4H), 1.55 (m, 4H), 1.23 (m, 20H), 0.86 (m, 6H); MS (FAB) 390.3 (M^{C+}), calc. for $C_{24}H_{38}S_2$: 390.

*1-(3-octylthiophene-2-yl)-3,5-dibromo benzene (**E′1.1**).* **E′1.1** was obtained from the synthesis of **E′1** when the reaction stopped spontaneously before completion. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.53 (d, $^4J = 1.6$ Hz, 2H, Ha2 and Ha6), 7.42 (t, $^4J = 1.7$ Hz, 1H, Ha4), 7.26 (d, $^3J = 5.1$ Hz, 1H, Hb2), 6.98 (d, $^3J = 5.1$ Hz, 1H, Hb3), 2.68 (m, 2H), 1.58 (m, 2H), 1.25 (m, 10H), 0.87 (m, 3H); MS (FAB) 430.0 (M^{C+}), calc. for $C_{18}H_{22}S_1Br_2$: 430.0.

*1,3-Bis(3-octylthiophene-2-yl)-5-bromobenzene (**E′1.2**).* **E′1.2** was obtained from the synthesis of **E′1** when the reaction stopped spontaneously before completion. ^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm) 7.62 (t, $^4J = 1.7$ Hz, 1H, Ha2), 7.50 (d, $^4J = 1.7$ Hz, 2H, Ha4 and Ha6), 7.26 (d, $^3J = 5.1$ Hz, 2H, Hb2), 6.97 (d, $^3J = 5.1$ Hz, 2H, Hb3), 2.62 (m, 4H), 1.59 (m, 4H), 1.25 (m, 20H), 0.87 (m, 6H); MS (FAB) 545.2 (M-1), calc. for $C_{30}H_{41}S_2Br$: 546.2.

*1,3-Bis(3-octylthiophene-2-yl)-5-methylbenzene (**E′1.2g**).* This byproduct was obtained from the purification of **E′1**. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.30 (m, 1H, Ha2), 7.24 (d, $^3J = 5.4$ Hz, 2H, Hb2), 7.21 (m, 2H, Ha4 and Ha6), 6.99 (d, $^3J = 5.4$ Hz, 2H, Hb3), 2.68 (m, 4H), 1.58 (m, 4H), 1.25 (m, 20H), 0.87 (m, 6H); MS (FAB) 481.4 (M+1), calc. for $C_{31}H_{44}S_2$: 480.3.

*1,3-Bis(3-octylthiophene-2-yl)-5-phenylbenzene (**E′1.2h**).* This byproduct was obtained from the purification of **E′1.** MS (FAB) 542.3 (M^{C+}), calc. for $C_{36}H_{46}S_2$: 542.5.

*Intermediate Molecules (**E6a.1** and **E6a.2**).* These molecules were obtained as described for **E6a** using 1.5 equiv of **L6c** for 1 equiv of tribromobenzene. The crude product (a mixture of **E6a**, **E6a.1**, and **E6a.2**) was purified by HPLC (Nucleosil columns) using a mixture of dichloromethane:hexanes (8:92) as eluent. **E6a.1:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.64 (d, $^4J = 1.6$ Hz, 2H), 7.54 (t, $^4J = 1.7$ Hz, 1H), 7.16 (s, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 6.82 (s, 1H), 2.79 (m, 20H), 2.57 (m, 4H), 1.69 (m, 24H), 1.28 (m, 120H), 0.88 (m, 36H); MS (FAB) 1436 (M^{C+}), calc. for $C_{78}H_{111}S_6Br_2Cl$: 1436. **E6a.2:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.67 (m, 1H), 7.62 (m, 2H), 7.21 (s, 2H), 7.02 (s, 2H), 6.98 (s, 2H), 6.97 (s, 2H), 6.95 (s, 2H), 6.82 (s, 2H), 2.80 (m, 20H), 2.57 (m, 4H), 1.69 (m, 24H), 1.28 (m, 120H), 0.88 (m, 36H); MS (MALDI-TOF) 2557, calc. for $C_{150}H_{219}S_{12}BrCl_2$: 2556.

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