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Simple Access to Sol–Gel Precursors Bearing Fluorescent Aromatic Core Units

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Di-, tri-, and tetrathienyl-substituted polycyclic aromatic fluorophores were prepared from different aryldi-, aryltri-, or aryltetrahalides by a simple and fast Suzuki coupling. The reaction was optimized for the synthesis of the desired materials on multigram scale. The coupled products were converted into the corresponding iodides through iodination with *N*-iodosuccinimide. The iodides turned out to be versatile starting materials for applications, such as periodic mesoporous organosilica syntheses. They were converted into a variety of new trimethoxysilyl arenes by using a very efficient Pd-mediated C–Si cross-coupling, which was also extended to the corresponding thienyl bromides by using a dimeric Pd^I catalyst. All compounds were characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and ATR-IR spectroscopy and HRMS.

Introduction

The development of organic and organic–inorganic hybrid materials and their application in energy conversion, for example, solar cells[1] and light-emitting thin films,[2] has recently received widespread attention in the scientific community. Covalently embedding functionalized organic moieties into an inorganic framework opens up a whole new field in material sciences. Aromatic and heteroaromatic compounds have been of interest for fundamental research in the past. Moreover, some of them have recently received major attention due to their combination of advantageous optical, electronic, chemical, and/or physical properties.[3] Recent advances in polymer chemistry particularly focus on thiophenes containing π-donor–acceptor pairs suitable for producing photoluminescent and energy-harvesting macromolecules.[4] These might be interesting for the development of new organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and polymeric optical fibers (POFs).[5] Experimental as well as theoretical approaches have shown that the fluorescence properties and MO energy gaps of aryl-bridged dithiophenes (2-thienyl)-(Ar)-(2-thienyl) can be tuned by modification of their aromatic core.[6] As our group is dedicated to the synthesis of new organic–inorganic hybrid materials, we took an interest in the idea of producing highly fluorescent compounds bearing (trialkoxysilyl)thiophene moieties as subunits for gelation.[7]

Results and Discussion

C–C Couplings

Intrigued by the progress in the field of polymer synthesis, we designed our reaction pathway accordingly: In a first step, a catalytic C–C bond formation would give us the 2-thienyl arenes that should be easy to isolate and purify, for example, by recrystallization, due to their planar structure and thermal stability. Subsequent Wohl–Ziegler iodination or bromination by using *N*-halosuccinimides would result in the formation of the 5-halo-2-thienyl arenes, the latter ones being the ideal candidates for Pd-mediated C–Si coupling.

Starting with the C–C coupling, we intended to avoid both Stille-type coupling of aryl halides with the rather expensive and toxic 2-(tributylstannyl)thiophene[8] as well as Kumada-type[9] or Negishi-type[10] couplings by using air- and moisture-sensitive Grignard or zinc organyls, respectively (Scheme 1).

Therefore, the first key step in the synthesis of the desired compounds was the Suzuki–Miyaura-type coupling of thiophene-2-boronic acid with different polycyclic aromatic halides **1**–**18a** to yield the corresponding thienyl-substituted products **1**–**15b** and **18b**. As many of the starting materials given in Figure 1 are scarcely available, we invested some time in finding the appropriate synthetic methods to obtain suitable amounts of the desired aryl halides.

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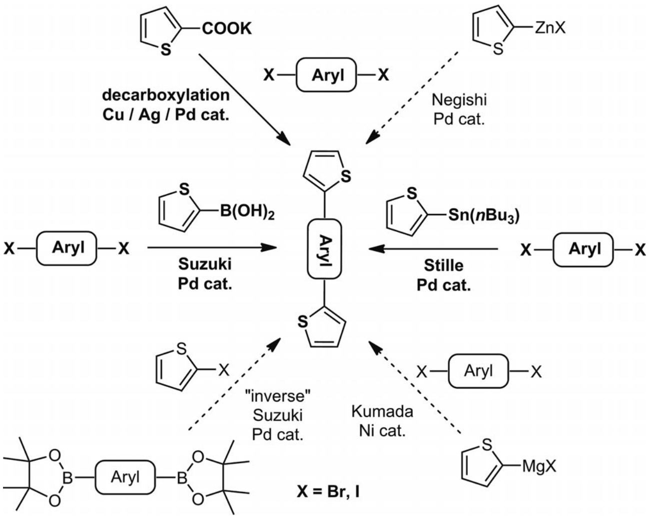


Scheme 1. Possible access to dithienyl-substituted arenes by different transition-metal-catalyzed coupling reactions. Pathways marked with dashed lines have not been explored in this work.

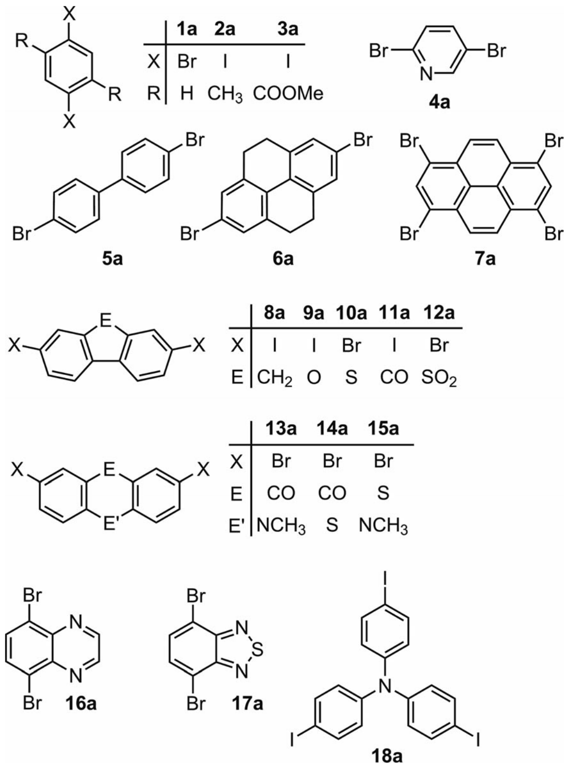


Figure 1. Starting materials for Suzuki–Miyaura coupling reactions.

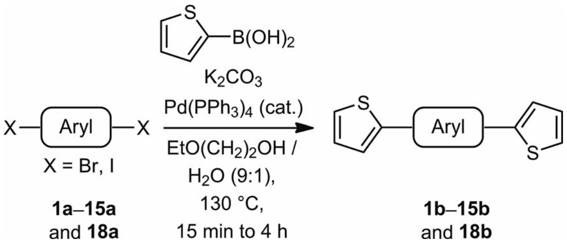
We could not produce larger quantities of 1,8-dibromopyrene due to poor selectivity in the dibromination of pyrene and the tedious workup by fractionated crystallization. Although noted otherwise in the literature, we could not accomplish a large-scale synthesis of 2,7-dibromopyrene starting from the reduced species THP (**6a**).[11] However, all other compounds were isolated in suitable yields without problems.

Suzuki–Miyaura couplings of aromatic and heteroaromatic halides with boronic acids have already been intensely studied. The reaction conditions have been optimized in terms of solvent, temperature, catalyst loading, and reaction time, turning the Suzuki coupling into a versatile and environmentally benign process.[12]

Our first goal was to apply a literature procedure to our polycyclic aromatic substrates. In order to efficiently perform batch reactions on a 20-mmol scale, we designed several criteria for the reaction set up which comprise (1) fast conversion of the starting materials (less than 1 h); (2) the ability to work under non-inert conditions; (3) the use of common solvents such as alcohol/water mixtures; (4) a simple workup.

The reaction variants we took from published preparations, for example, by using *n*-butanol/H_2O (7:1)/K_3PO_4,[13] failed to give the products within the desired reaction time due to incomplete conversion. Appealed by the concept of "naked" Pd catalysts,[14] we tried to establish a new procedure which would meet our expectations. Employing $Pd(PPh_3)_4$ as a comparatively cheap Pd source and potassium carbonate as a base (scheme in Table 1), we identified a 9:1 mixture of ethoxyethanol/water to be the ideal solvent to obtain the dithienyl derivatives in moderate to excellent yields. Using other solvents such as THF/H_2O (1:1) gave poorer yields.

Table 1. Scope of the newly developed Suzuki coupling protocol for the synthesis of thienyl-substituted aromatics.[a]



Product	Yield [%][b]	Product	Yield [%][b]
1b	98	**9b**	87
2b	74	**10b**	97
3b	83[c]	**11b**	81
4b	58	**12b**	97
5b	73	**13b**	95
6b	89	**14b**	44
7b	98[d]	**15b**	85
8b	85	**18b**	90

[a] Reaction conditions: Aryl dihalide (20 mmol), 2-thienylboronic acid (44 mmol), K_2CO_3 (88 mmol), $Pd(PPh_3)_4$ (0.08 mmol), ethoxyethanol/H_2O (135:15 mL), 130 °C, 15 min. [b] Isolated yield of the product after recrystallization and workup of the mother liquor. [c] Using NEt_3 (80 mmol) and K_2CO_3 (8 mmol) as base. [d] Reaction on 1-mmol scale, 1.0 mol-% Pd, diglyme/ethoxyethanol/H_2O (20:20:5 mL), 150 °C, 4 h.

After careful optimization, we developed a protocol for the efficient conversion of the aryl halides, requiring a catalyst loading as low as 0.2 mol-% per reactive moiety. Only in the case of very poorly soluble tetrabromopyrene **7a** was it necessary to apply forcing conditions, using diglyme/

ethoxyethanol/H_2O (4:4:1) and higher catalyst loadings of 1.0 to 1.5 mol-%. The results of our work on the new coupling variant are summarized in Table 1.

Notably, the reaction does not require inert conditions, as it proceeds very rapidly and, to our best knowledge, mostly produces no significant amounts of interfering by-products. In terms of conversion, our results match the outcome of microwave irradiation experiments carried out by others, as the products started to precipitate within a few minutes.[15] In systematic studies, we discovered that replacing potassium carbonate with organic bases such as NEt_3 did not lower the conversion; however, it slowed down the reaction rate. Base-sensitive 2,5-diiododimethyl terephthalate (**3a**) was therefore successfully coupled in the presence of an excess amount of NEt_3 and substoichiometric quantities of K_2CO_3. We further observed that the reaction mostly proceeded smoothly at temperatures between 100 and 130 °C.

When exploring the substrate reactivity, we found electron-poor arenes such as the biphenyl derivatives **5a**, **6a**, and **8a**, ketone **11a**, and sulfoxide **12a** to be the most reactive ones. A significant turnover was detected for those compounds even below 100 °C. Arenes bearing electron-rich functional groups such as nitrogen- or sulfur-containing heterocycles (i.e., **13a** and **14a**, respectively) needed to be heated above 130 °C to react smoothly. In the case of **14a**, the decrease in reactivity might have led to the lower yield that was observed. This tendency is supported by the outcomes of the couplings of **1a** to **4a**: relatively electron-deficient dithienyl arenes featuring phenylene (**1a**) and bis(carboxymethyl)phenylene (**3a**) moieties were obtained in higher yields than electron-richer xylenes (**2a**) and pyridines (**4a**). Contrary to the reactions' dependency on the structure of the arenes, there was no significant difference between aryl bromides and aryl iodides.

A principal driving force of the reaction can be seen in the poor solubility of the products in the polar solvent mixture caused by the planarity and the extensive π-stacking of the emerging large aromatic molecules.

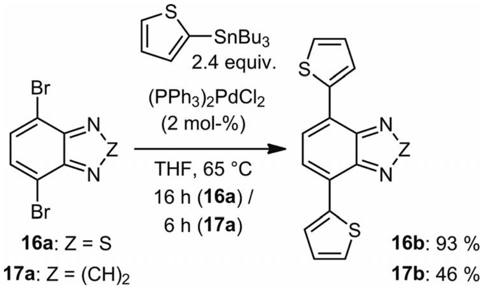
We successfully isolated 1,4-dithienylbenzene (**1b**) in excellent yields of around 98% after carrying out the reaction at 1 to 20-mmol scales and in a moderate yield of 51% at 50-mmol scale. When further increasing the amount of the dihalide up to 100 mmol, yields tended to be no longer reproducible but were very low in general, as no sufficient heating could be applied within the short reaction time given. As Pd^0 species generated in situ seem to be most reactive within the very first minutes of the conversion, proper heating of the reaction vessel might be crucial to rapidly generate the required amounts of catalyst while at the same time ensuring that the boronic acid does not undergo unwanted side reactions, such as protodeborylation.[16]

Several 10-mmol test reactions using $Pd(OAc)_2$ or immobilized Pd EnCat 40 as metal sources and PPh_3 as ligand under otherwise unchanged conditions furnished desired compound **1b**, however, in lower isolated yields of 22% for the homogeneous and 6% for the heterogeneous version. As we assumed a certain, yet limited, stability of $Pd(PPh_3)_4$ to be decisive for our reaction system, this outcome was in coherence with our expectations. Although the isolated yields of these reactions have been further improved by optimization of the reaction set up and workup, we consider the method given above as being the far more advantageous one, especially when compared to the methods presented in the literature.[17]

Testing the versatility of our method, we were able to readily obtain **13b** and **18b**, which, to the best of our knowledge, have not been prepared by Suzuki coupling before. However, we experienced some minor drawbacks: The procedure could not be applied to N-heterocycles, such as 3,6-dibromo-9-methyl-9*H*-carbazole[18] or 3,8-dibromo-1,10-phenanthroline,[19] giving only trace amounts of product and otherwise yielding an inseparable black tar. 9,10-Dibromoanthracene[20] and *p*-dibromoveratrole were unreactive under the given conditions, as they were recovered in about 80–85% yield.

Similarly, all attempts to synthesize dithienyl-substituted quinoxaline **16b** or benzothiadiazole **17b** through Suzuki coupling failed, as we mostly recovered only larger amounts of the unchanged dihalide. Compound **17a** has been reported to undergo Suzuki[21] and Sonogashira reactions,[22] but did not react to **17b** even when prolonging the reaction time up to 24 h under inert conditions. The reason for all these incompatibilities may lie in the electron-rich aromatic cores of both the dihalides and thiophene-2-boronic acid, making it nearly impossible for Pd^0 to undergo the common cycle of oxidative addition and reductive elimination. Other structural aspects, such as the diimino moieties of **16a** and **17a**, may also contribute to this behavior, requiring a highly reactive catalyst and/or thienyl species.

A complementary approach to the desired product through decarboxylative cross-coupling of **17a** with potassium 2-thienyl carboxylate at elevated temperatures[23] by using quinoline was not successful either. Hence, **16b** and **17b** were prepared by Stille coupling by using thienyl tri-*n*-butylstannane and $Pd(PPh_3)_2Cl_2$ as a catalyst (Scheme 2).[24]



Scheme 2. Stille coupling towards thienyl-substituted diimino derivatives. Yields for the isolated product are given.

The yield of the resulting crystalline crude products obtained by Stille coupling are comparable to those of the above-mentioned Suzuki reactions; however, the preparation of larger amounts of the thiophene-containing molecules was laborious, as it was hard to completely remove the tin organyls from the crude reaction mixtures by recrystallization. Further experiments will be conducted to solve this problem, for example, by treatment with EDTA[25] or adsorption on silica.

Fluorescence Data of the Dithienyl Arenes

Oligothiophenes are not only known for having semiconducting properties but also for their strong luminescence when exposed to UV light. Some of the thienyl arenes presented herein have already proven to be useful in energy harvesting and light conversion applications (see the Supporting Information). We were therefore pleased to detect blue to orange fluorescence during the Suzuki coupling. For a selection of samples the absorption and fluorescence spectra are shown in Figures 2 and 3, and the corresponding absorption and emission maxima are given in Table 2. The spectra of the remaining compounds are given in the Supporting Information.

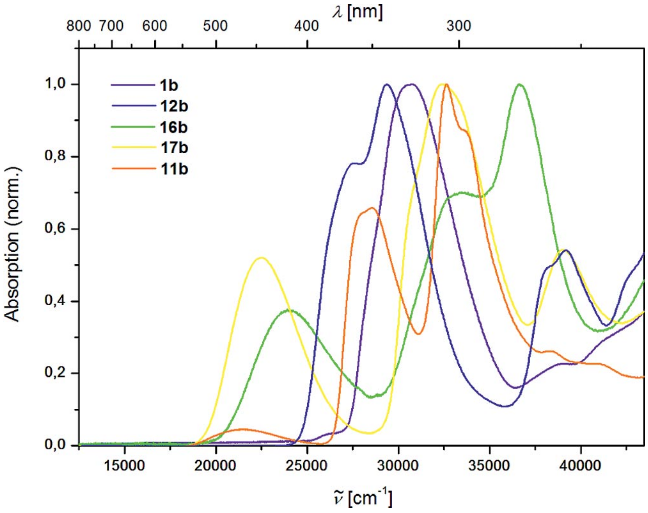


Figure 2. Absorption spectra of **1b**, **11b**, **12b**, **16b**, and **17b** solvated in CH_2Cl_2.

Table 2. Absorption and emission maxima and Stokes shift.

Substance	$\lambda_{abs,max}$ [cm^{-1}]	$\lambda_{em,max}$ [cm^{-1}]	Stokes shift [cm^{-1}]
1b	30675	26110	4565
11b	32637	16892	15745
12b	29360	22989	6371
16b	36630	18450	18090
17b	32510	17699	14811

The shown absorption spectra (Figure 2) cover a region from 230 up to 550 nm with a strong structured shape. It can be observed that the structure of the absorption spectra depends both on the binding motifs between the aromatic or heterocyclic systems and the use of different functional groups.

A single bond between the aromatic systems seems to lead to a less-structured spectrum (i.e., for **1b**), and annulation of the aromatic systems results in an overlap of two or more distinct absorption bands (i.e., for **11b**, **12b**, **16b**, and **17b**). Additionally, a large aromatic system or heterocyclic systems lead to a redshift in the absorption. The same effect is observed by insertion of a C=O group. Thus, it can be concluded that different absorption regions can be obtained through systematic control of the structural arrangements.

The emission spectra of these substances show a great variety (Figure 3) even if most substances emit in the range from 380 to 600 nm. In general, the emission spectra are less structured than one would expect from the absorption spectra, and variation of the excitation wavelength does not result in any changes in the emission spectra due to the fluorescence from the lowest excited state.

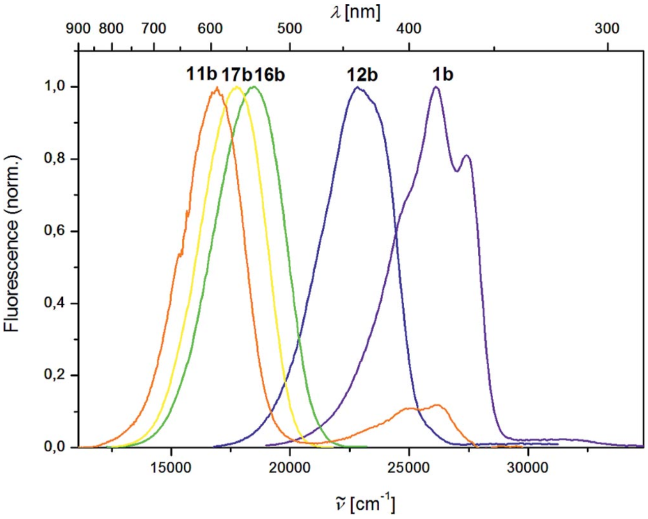


Figure 3. Emission spectra of **1b**, **11b**, **12b**, **16b**, and **17b** solvated in CH_2Cl_2. Excitation wavelengths: **1b**: λ_{ex} = 272 nm, **11b**: λ_{ex} = 321 nm, **12b**: λ_{ex} = 305 nm, **16b**: λ_{ex} = 335 nm, **17b**: λ_{ex} = 275 nm.

The influence of the structure on the emission is similar to that discussed for the absorption properties. As well as for the absorption spectra, the position of the emission can be controlled by the binding motif between the aromatic or heterocyclic system. A further method to get the emission to the desired region is the use of heteroatoms or functional groups (e.g., carbonyl, ester, or amino groups) whereupon the influence of the carbonyl group on the emission properties can be weakened by inserting another functional group. The influence of the functional groups can also be analyzed by the Stokes shift of the compounds, and here again a large Stokes shift is observed for compounds containing the above-mentioned functional groups.

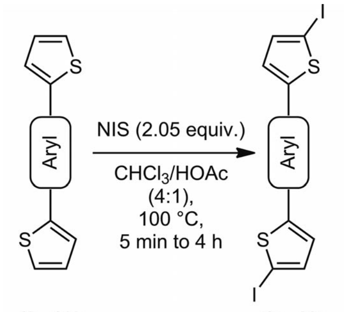
Two of the substances, **16b** and **17b**, were iodinated, and the spectra are shown in Supporting Information. It is found that the iodination leads to a redshift in the absorption spectra and emission spectra. Additionally, for the iodinated substances a stronger structured absorption spectrum is found and an additional emission band at a lower wavelength. For compound **7b** (a pyrene derivative), an excimer was also detected.

Thus, by means of the absorption and emission spectra of the 20 substances the influence of binding motifs as well as heteroatoms or functional groups on the absorption and emission properties can be discussed, and with this information the spectroscopic properties of the dyes can be adapted to the designated application.

Iodination of Arylated Thiophenes

As thiophene preferably reacts with radical species at its acidic 2- and 5-positions, we could easily synthesize iodides **1c**–**14c** and **16c**–**18c** by modifying the procedure of Cao et al.[24] and by replacing NBS with NIS (Table 3). The presence of glacial acetic acid in the reaction mixture was identified to be crucial for rapid conversion of the starting material; however, a 1:1 mixture of HOAc/chloroform as reported was not required. Due to the very low solubilities of most products, they were obtained as precipitates from the hot reaction mixture during or shortly after the dissolving of the iodination agent. Only in some cases, such as for the more-soluble 2,5-bis(5-iodothien-2-yl)-1,4-dimethylbenzene (**2c**) did the chloroform have to be removed before filtering to obtain a precipitate.

Table 3. Scope of the selective iodination of aryl-substituted thienyl halides in the 5-position by using *N*-iodosuccinimide (NIS).[a]



1b–**18b**
except **15b**

1c–**18c**
except **15c**

Product	Yield [%][b]	Product	Yield [%][b]
1c	90	**10c**	84
2c	80	**11c**	89
3c	84	**12c**	76
4c	71	**13c**	70
5c	80	**14c**	96
6c	98	**16c**	93
7c	99[c]	**17c**	98
8c	87	**18c**	96
9c	73		

[a] Reaction conditions: Dithienyl arene (5 mmol), NIS (10.3 mmol), $CHCl_3$/HOAc (20:5 mL), 100 °C, 5 min. [b] Isolated yield. [c] Reaction performed on 1-mmol scale, NIS (8.00 mmol), pure HOAc, 130 °C, 4 h.

In most cases, the substitution of the thienyl protons with iodine, as expected, led to an immediate quenching of the intense (violet to orange) fluorescence observed in the reaction mixtures. Only for compounds **16c** and **17c** did we find a reduced yet still remarkable emission of light, which could be attributed to different fluorescence properties of those electron-rich arenes (see spectra in the Supporting Information).

Contrary to the mild reaction conditions and the minimal excess of NIS employed in most of the aforementioned syntheses, the tetraiodination of **7b** was achieved only by heating the starting material in pure acetic acid together with an excess amount of NIS. Most of the poorly soluble iodides were recrystallized from DMF, DMSO, or, in case of **7b**, large amounts of *o*-dichlorobenzene. However, the yields were lowered significantly (approx. 20% overall loss) by each recrystallization step. Comparing the NMR spectra of some crystalline samples, which showed minor impurities, to the ones of the crude products, we assume that in many cases there is no need for further purification. The byproducts are most likely to be generated under the harsh conditions necessary for recording the spectra ([D_6]DMSO at 100–120 °C).

Phenothiazine derivatives are readily oxidized to form stable paramagnetic radical cations.[26] Therefore, the only arylthiophene that could not be iodinated with NIS was **15b**, yielding a deep purple precipitate which we were not able to re-reduce to the free amine, neither by simple recrystallization from DMF/H_2O nor by using ascorbic acid.[27] Other attempts to prepare **15c** by metalation with *n*BuLi and addition of I_2 at low temperatures or by electrophilic iodination by using ICl and potassium acetate at 25 °C failed.[28]

The crystal structure of diiodide **16c** is shown in Figure 4. Crystals of suitable quality were obtained from a dichloromethane solution of the crude product by slow evaporation of the solvent over weeks. Selected bond lengths and angles prove that the dithienylarenes exhibit a quasilinear and rigid structure. The planarity of the aromatic system, which might be dependent on the substitution of the central phenylene unit, is only slightly broken in the case of **16c** (for further details on the X-ray structure analysis, see the Supporting Information).

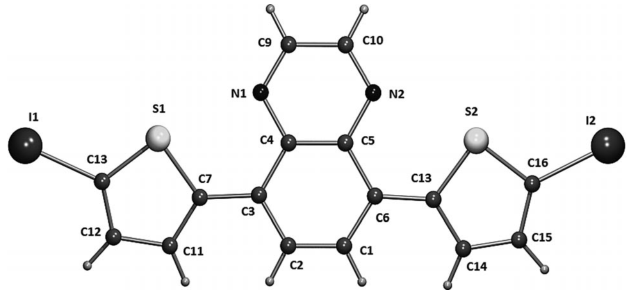


Figure 4. Molecular structure of **16c** in the solid state determined by X-ray single-crystal diffraction (ball-stick model). Selected bond lengths [Å]: C3–C7 1.46, C6–C8 1.48, C4–N1 1.36, C7–S1 1.74, C9–C10 1.42, C12–C13 1.40, C13–I1 2.07. Selected angles [°] and dihedral angles [°]: C8–S2–C16 90.9, C4–N1–C9 117.4, C2–C1–C6 122.0, C6–C8–C14 123.9, S2–C16–I2 119.6; C4–C3–C7–S1 8.3, C5–C6–C8–S2 12.6.

C–Si Couplings

Although being a versatile tool for the synthesis of noncommercially available aryltrialkoxysilanes, the palladium-catalyzed carbon–silicon bond-forming reaction between aryl halides and trialkoxysilanes $HSi(OR)_3$ (R = Me, Et) has not yet been exceedingly covered in the literature. Since its discovery in the late 1990s, this σ-bond metathesis-type reaction[29] was further developed by Manoso and DeShong[30] as well as by Masuda et al., who also presented a rhodium-mediated version.[31] The main reason for the comparatively minor attention this reaction has received up to now might be its rather limited scope of starting materials, comprising only several aryl iodides and electron-rich aryl bromides, and its tendency to give considerable amounts of undesired byproducts, especially by reductive proto-dehalogenation.

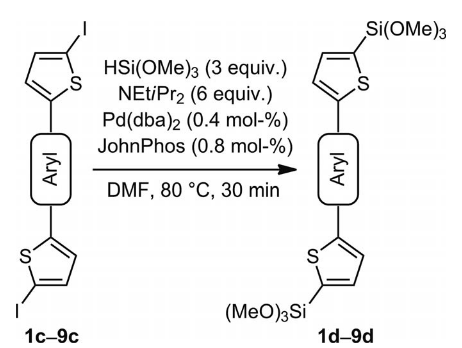
Furthermore, the reaction products are moisture sensitive and can be purified only to a very limited extent. The variety of functional groups and the high molecular weight of the aromatics presented here make it even more difficult to pursue common purification methods, for example, bulb-to-bulb distillation. As we initially wanted to synthesize unknown 4,7-bis[5-(trimethoxysilyl)thien-2-yl]benzo[*c*][1,2,5]-thiadiazole (**17d**), we focused on developing suitable conditions for the coupling of **17c** with trimethoxysilane or triethoxysilane.

We based our initial screening on the protocol of Manoso and DeShong, employing NMP as a polar aprotic solvent and $Pd(dba)_2$/Johnphos (di-*tert*-butylphosphanylbiphenyl) as catalyst.[30] In contrast to the literature, aqueous workup of the obtained solutions was not feasible, because extraction with pentane and washing with deionized water yielded only inseparable mixtures of polymerized material. Furthermore, the use of triethoxysilane yielded at best the dehalogenated starting materials. Changing the solvent to DMF and/or altering the reaction temperatures showed no beneficial effect. A test reaction with **16c** performed in quinoline as basic solvent and using $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ as the catalyst had a similar outcome, as **16b** was recovered in 78% yield.

Finally, we replaced triethoxysilane with trimethoxysilane, which led to a decisive improvement in reactivity. By carrying out the reaction in DMF and at modest temperatures, full conversion of the aryl iodides was observed within 2 h at 60 °C or within 30 min at 80 °C (Table 4). This way, the amount of catalyst was reduced to only 0.2 mol-% Pd per thiophene moiety, which corresponds to less than 10% of the figures given in the literature.[30] After a simple workup, which included filtering off the inorganic salts and removing the oxidized ligand by adsorption on Na_2SO_4, the desired sol–gel precursors were reproducibly isolated in excellent to almost quantitative yields. When scaling up the synthesis of **1d** to 20 mmol, we noticed that the reaction became clearly exothermic during the first minutes and further proceeded without any change in product distribution or purity.

Because the obtained sol–gel precursors formed highly viscous waxes, they tended to trap the solvent inside their matrix. Furthermore, they readily polymerize when heated or when stored for a longer time. The outcome of the experiments given in Table 4 nevertheless indicates a very broad applicability of the optimized procedure.

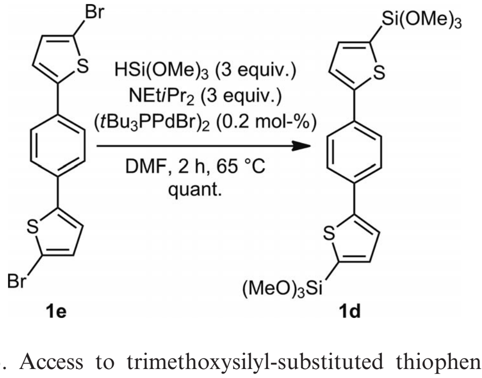
Table 4. C–Si cross-coupling reactions of 5-iodothien-2-yl-functionalized aromatics to the corresponding bis(trimethylsilyl) derivatives.[a]



Product	Yield [%][b]	Product	Yield [%][b]
1d	98	**8d**	70
2d	98	**11d**	88
3d	91	**13d**	69
4d	85	**16d**	97
5d	92	**17d**	94
6d	98	**18d**	98

[a] Reaction conditions: Di- or trithienyl halide (1 mmol), $Pd(dba)_2$ (0.40 mmol), JohnPhos (0.80 mmol), $HSi(OMe)_3$ (1 mmol), DIPEA (3 mmol) per halide moiety, DMF (5 mL), 80 °C, 30 min. [b] Isolated yield (90 to 95% purity according to ^1H NMR).

Having developed an efficient method for the synthesis of trimethoxysilylarenes from thienyl iodides, we sought the activation of the much cheaper thienyl bromides. Because the corresponding aryl bromides turned out to be even less soluble in DMF than the aryl iodides, no conversion was observed after 2 h at 60 °C under otherwise unchanged conditions. A stepwise increase in the temperature and/or the reaction time up to 120 °C and 16 h furnished only the dehalogenated species. The use of more electron-rich and more sterically demanding phosphanes such as XPhos[32] and BrettPhos[33] did not alter these results. However, we were finally able to convert 1,4-bis(5-bromothien-2-yl)benzene (**1e**) into desired silylated product **1d** in quantitative yield and with an excellent selectivity by employing the highly active Pd^I dimer $(tBu_3PPdBr)_2$ (Scheme 3).



Scheme 3. Access to trimethoxysilyl-substituted thiophenes from their corresponding bromides by using a highly active dimeric Pd^I catalyst.

This catalyst has been reported to facilitate C–C, C–N, and C–S bond formations,[34] but it has never been used for the coupling of aryl halides with trialkoxysilanes. The low catalyst loadings of only 0.1 mol-% per halide moiety outweigh the relatively high costs of this Pd dimer. Experiments are under way to explore the applicability of this protocol to the synthesis of trialkoxysilanes from other aryl and heteroaryl halides.

Conclusions

We have presented access towards fluorescent sol–gel precursors incorporating various functional groups by using a simple and reliable three-step synthesis, covering a considerable scope of readily available polycyclic aromatic compounds. The Suzuki coupling we introduced herein features an optimized workup which enabled us to produce larger amounts of thiophene-substituted arenes with no need for column chromatography.

We further accomplished the iodination of thienyl arenes, although still encountering problems for redox-sensitive phenothiazines. The iodides did not only to some extent show some interesting luminescence properties themselves but could also most conveniently be converted into the desired (trimethoxysilyl)thienyl arenes. The C–Si bond formation proceeds quantitatively with all tested substrates, although the isolated yields, in some cases, might slightly vary depending on the workup. We therefore could accomplish our goal of using the special reactivity of the thiophene moieties to generate a variety of new arylsilanes.

Because the new bis(trimethoxysilylthienyl) arenes we described are rather sensitive when exposed to air or in solution and might also be able to react with silica gel and quartz surfaces, we currently are undertaking great efforts to determine their luminescence properties. The UV/Vis and fluorescence spectra will then be compared to those of the non-silylated arenes. We may already point out that their fluorescence in solution most likely does not significantly differ from the data presented herein. However, some of the above-mentioned compounds feature a different fluorescence behavior in the solid state, which will be investigated with respect to the method of deposition on several surfaces. Figure 5 gives a first impression on the different fluorescence intensities and colors of the silanes that are observed in solution.

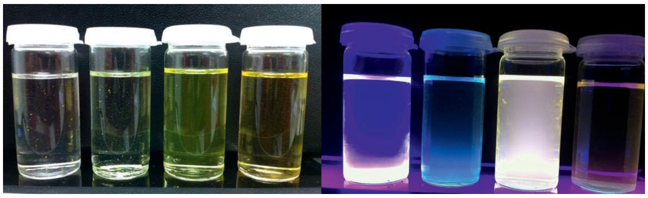


Figure 5. Appearance of (trimethoxysilylthienyl)silane solutions in DCM under normal and UV light (λ_{ex} = 254/366 nm; from left to right: **6d**, **13d**, **16d**, and **11d**).

We might soon be able to create sol–gel precursors carrying nearly every desired functional group and will then proceed with the sol–gel synthesis of new hybrid organosilica and xerogels, characterize their molecular structure, and explore the possible use of these silicates in optics, electronics, sensors, and heterogeneous catalysis, for example, as superhydrophobic acidic materials for the esterification of fatty acids.

In the long run, the quasilinear dithienyl halides and silanes described above might be useful in the synthesis of organic linkers for metal–organic frameworks (MOFs) by Pd-catalyzed carboalkoxylation,[35] serve as organic building blocks in Hiyama cross-couplings,[36] or help to develop new high-performance hybrid polymers.[37]

Experimental Section

General: Compounds **1a**, **4a**, **5a**, and **6a** and all other chemicals necessary for the syntheses of the Suzuki reaction substrates as well as for the reaction sequences presented herein were purchased from Sigma–Aldrich, Acros Organics, Maybridge, and VWR and used as received. Dry DMF was supplied by Acros Organics, whereas THF, pentane, toluene, Et_2O, and CH_2Cl_2 were dried prior to use according to standard procedures.[38] Liquid phase ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded with two Bruker Spectrospin devices with a resonance frequency of 400 or 600 MHz, 151 or 101 MHz, and 76 MHz for the ^1H, ^{13}C, and ^{29}Si nuclei, respectively. The spectra are internally referenced to $SiMe_4$. The infrared spectra with a resolution of $\pm 2\,cm^{-1}$ were recorded by using a PerkinElmer FT-ATR IR 1000 spectrometer equipped with a diamond coated ZnSe-window. High-resolution mass spectra were obtained in EI+ mode with a Waters GCT Premier spectrometer. MALDI-ToF measurements were conducted with a Bruker Daltonics Ultraflex spectrometer with CHCA (α-cyano-4-hydroxycinnamic acid) being the matrix compound. The UV/Vis absorption and fluorescence of the precursor were measured by using a Perkin–Elmer Lambda 900 and a Horiba Jobin–Yvon Fluorolog 3–22 τ in steps of 0.1 and 1.0 nm, respectively; the SiO_2 cuvettes used had a width of 1.0 cm.

Absorption and Emission Spectra: All substances were diluted in dichloromethane purchased from Merck in Uvasol quality. The concentration of the solutions used for the absorption spectra was in the range of $10^{-5}\,mol\,L^{-1}$, for the fluorescence measurements in the range of $10^{-6}\,mol\,L^{-1}$. Absorption spectra were recorded with a Perkin–Elmer Lambda 950 UV/Vis/NIR double beam spectrophotometer, emission spectra were recorded with a Jobin–Yvon FluoroMax2 spectrophotometer. The cuvettes used for absorption measurements were cylindrical quartz cuvettes with a path length of 1 cm, for emission measurements a 1 cm × 1 cm quartz cuvette was used.

X-ray Structure Analyses: Crystal data and refinement parameters for compound **16c** are collected in Table 5. The structure was solved by direct methods (SHELXS97), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. For **16c**, a semiempirical absorption correction (Multiscan) was carried out. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model.

CCDC-864482 (for 1**6c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses of the Suzuki Reaction Substrates: The full procedures are only given if appropriate.

Table 5. Summary of the crystallographic data and details of data collection refinement.

	16c
Empirical formula	$C_{16}H_8I_2N_2S_2$
Formula weight [g mol^{-1}]	546.16
Crystal size [mm^3]	0.14 × 0.10 × 0.06
T [K]	150(2)
λ [Å]	1.54184
Crystal system	monoclinic
Space group	$C2/c$
a [Å]	34.1122(17)
b [Å]	5.7372(2)
c [Å]	18.5596(9)
α [°]	90
β [°]	118.376(7)
γ [°]	90
V [Å^3]	3195.8(2)
Z	8
$\rho_{\text{calcd.}}$ [g cm^{-1}]	2.270
μ [mm^{-1}]	33.362
θ-range [°]	2.94–62.67
Reflections collected	9434
Independent reflections	2551 [$R_{\text{int.}}$ = 0.0416]
Data/restraints/parameters	2551/0/199
Final R indices [$I > 2\sigma(I)$][a]	0.0337/0.0812
R indices (all data)	0.0356/0.0823
GooF[b]	1.077
$\Delta\rho_{\text{max/min}}$ [e Å^{-3}]	0.591/–2.126

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o)^2]^{1/2}$. [b] GooF = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

2,5-Diiodo-1,4-dimethylbenzene (2a):[39] Prepared in 75% yield from *p*-xylene as colorless crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.67 (s, 2 H), 2.36 (s, 6 H) ppm. HRMS: calcd. for $C_8H_8I_2$ 357.8716; found 357.8709.

2,5-Diiododimethyltherephthalate (3a):[40] Prepared in three steps with a total yield of 16% from **2a**. The yield was limited due to the laborious workup of the thick MnO_2 slurry obtained at the end of the oxidation steps. Esterification of 2,5-diiodotherephthalic acid: $SOCl_2$ (2.3 equiv., 2.97 g, 25.0 mmol, 1.81 mL) was added dropwise to MeOH (100 mL). The solution was stirred at 25 °C for 2 h. The acid (4.60 g, 11.0 mmol) was added. The resulting suspension was heated to 70 °C under reflux conditions for a further 8 h. The formed solid was filtered at –18 °C, dried in the vacuum, and recrystallized from MeOH/CH$_2$Cl$_2$ (1:1) to yield **3a** (2.80 g, 6.30 mmol, 57%) as colorless crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.35 (s, 2 H), 3.97 (s, 6 H) ppm. HRMS: calcd. for $C_{10}H_8I_2O_4$ 445.8512; found 445.8500.

1,3,6,8-Tetrabromopyrene (7a):[41] Prepared in 98% yield from pyrene as a colorless solid. The crude product, being very poorly soluble in all available solvents except for boiling PhNO$_2$, was used without purification and only characterized by HRMS: calcd. for $C_{16}H_6Br_4$ 513.7203; found 513.7189.

2,7-Dibromo-4,5,9,10-tetrahydropyrene (6a):[11] Prepared in two steps with a total yield of 32% from pyrene as colorless crystals. The yield was limited due to several recrystallization steps in both of the stages. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.22 (s, 4 H), 2.83 (s, 8 H) ppm. HRMS: calcd. for $C_{16}H_{12}Br_2$ 363.9286; found 363.9286.

3,6-Diiodo-9*H*-fluorene (8a):[42] Prepared in 57% yield from 9-*H*-fluorene as colorless crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.80 (s, 2 H), 7.62 (d, 2 H), 7.41 (d, 2 H), 3.75 (s, 2 H) ppm. HRMS: calcd. for $C_{13}H_8I_2$ 417.8716; found 417.8707.

2,8-Dijododibenzo[*b*,*d*]furan (9a):[43] Prepared in 38% yield from dibenzo[*b,d*]furan as colorless crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.12 (d, 2 H), 7.66 (dd, 2 H), 7.25 (d, 2 H) ppm. HRMS: calcd. for $C_{12}H_6I_2O$ 419.8508; found 419.8550.

2,8-Dibromodibenzo[*b*,*d*]thiophene (10a):[44] Prepared in 34% yield from **12a** as colorless crystals. The yield was limited due to difficulties with the phase separation after quenching the reaction with H$_2$O. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.82 (dd, 2 H), 7.68–7.61 (m, 2 H), 7.53 (t, 2 H) ppm. HRMS: calcd. for $C_{12}H_6Br_2S$ 339.8557; found 339.8585.

2,7-Diiodo-9*H*-fluoren-9-one (11a):[45] Prepared in 68% yield from 9*H*-fluoren-9-one as orange crystals. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.95 (d, 2 H), 7.83 (dd, 2 H), 7.25 (d, 2 H) ppm. HRMS: calcd. for $C_{13}H_6I_2O$ 431.8508; found 431.8488.

2,8-Dibromodibenzo[*b*,*d*]thiophene-5,5-dioxide (12a):[44] Prepared in two steps with a total yield of 72% from dibenzo[*b,d*]thiophene as colorless crystals. ^{1}H NMR (600 MHz, 100 °C, [D$_6$]DMSO): δ = 8.15 (s, 2 H), 8.09 (d, 2 H), 8.00–7.94 (m, 2 H) ppm. HRMS: calcd. for $C_8H_8I_2$ 371.8455; found 371.8456.

2,7-Dibromo-10-methylacridin-9(10*H*)-one (13a):[2,18,46] Prepared in three steps with a total yield of 56% from *N*-phenylanthranilic acid as yellow crystals. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.42 (s, 2 H), 7.93 (d, 2 H), 7.80 (d, 2 H), 3.93 (s, 3 H) ppm. HRMS: calcd. for $C_{12}H_6Br_2O_2S$ 364.9051; found 364.9049.

3,6-Dibromo-9*H*-thioxanthen-9-one (14a):[47] Prepared in 60% yield from 9*H*-thioxanthen-9-one as bright yellow crystals. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 8.51 (s, 2 H), 7.88 (d, 2 H), 7.74 (d, 2 H) ppm. HRMS: calcd. for $C_{13}H_6Br_2OS$ 367.8506; found 367.8511.

2,7-Dibromo-10-methyl-10*H*-phenothiazine (15a):[48] Prepared in two steps with a total yield of 42% from 10*H*-phenothiazine as colorless crystals. Bromination of the *N*-methylated derivative using NBS was done in DMF for 1 h at 80 °C and 24 h at 25 °C (similar to **13a**), followed by quenching with H$_2$O and recrystallization from EtOH/CHCl$_3$. Even samples pure in NMR can be dark purple in color due to minor radical cation impurities. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31–7.20 (m, 2 H), 6.65 (d, 1 H), 3.31 (s, 2 H) ppm. HRMS: calcd. for $C_{13}H_9Br_2ONS$ 368.8822; found 368.8817.

5,8-Dibromoquinoxaline (16a):[49] Prepared in two steps with a total yield of 39% from **17a** as golden crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.04 (s, 2 H), 8.02 (s, 1 H) ppm. HRMS: calcd. for $C_8H_4Br_2N_2$ 285.8721; found 285.8727.

4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (17a),[50] Prepared in two steps with a total yield of 71% from *o*-phenylenediamine as grayish crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75 (s, 2 H) ppm. HRMS: calcd. for $C_6H_2Br_2N_2S$ 291.8305; found 291.8318.

Tri(4-iodophenyl)amine (18a):[51] Prepared in 61% yield from triphenylamine as colorless crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.56 (d, 6 H), 6.83 (d, 6 H) ppm. HRMS: calcd. for $C_{18}H_{12}I_3$ 622.8104; found 622.8079.

Standard Suzuki Coupling Procedure: Thiophene-2-boronic acid (5.63 g, 44.0 mmol, 2.20 equiv.) was mixed with the aromatic dihalide (20.0 mmol) and K$_2$CO$_3$ (12.1 g, 88.0 mmol, 4.40 equiv.) in ethoxyethanol/deionized water (9:1, 150 mL). Pd(Ph$_3$)$_4$ (94.0 mg, 8×10^{-5} mol, 0.4 mol-%) was added to the stirred suspension, which was then heated *rapidly* to 130 °C and maintained under reflux conditions for 15 min. The resulting solution darkened and mostly became black very shortly after reaching the boiling point, the crude product precipitating either directly or on cooling of the reaction mixture to 25 °C. Deionized water (200 mL) was added at room temperature to precipitate the main part of the product and to dissolve the formed salt as well as the remaining starting materials. After stirring thoroughly for 1 h, the solid was filtered off, washed with ethanol (3 × 20 mL) and dried in vacuo. The dithienyl compounds were obtained in 90 to 95% purity, as determined by ^{1}H NMR spectroscopy. Analytically pure samples were obtained by recrystallization from DCM/EtOH (2:1), DMSO, or toluene/DMF (2:1, 1:1 or 1:2), depending on the different solubilities of the compounds. The mother liquors of the recrystallizations were partly evaporated and cooled to –18 °C to yield more of the products, which were then filtered and dried in vacuo.

Standard Iodination Procedure: A stirred suspension of the thienyl-substituted aromatic (5.00 mmol) in HOAc/$CHCl_3$ (1:4, 25 mL) was treated with *N*-iodosuccinimide (1.16 g, 5.15 mmol, 1.03 equiv. per thiophene moiety). The reaction mixture was then heated *rapidly* under reflux conditions to 90 °C for 5 min. During that time, all of the NIS dissolved. The crude products were mostly obtained as precipitate from the dark red to orange colored solutions either directly or on cooling. Otherwise, the chloroform was removed by rotary evaporation to obtain a suspension of the solid crude product. After stirring for 1 h at 25 °C, it was filtered off, washed with EtOH (3 × 20 mL), and dried in vacuo. Analytical samples of the mostly microcrystalline solids were obtained by recrystallization from DMF, or, preferably, from DMSO (exception **7b**: *o*-dichlorobenzene).

Standard C–Si Coupling Procedure: A flame-dried Schlenk flask was flushed with nitrogen and charged with dry DMF (5 mL). A fine mixture of $Pd(dba)_2$ (1.2 mg, 2.0×10^{-6} mol, 0.20 mol-%) and JohnPhos (1.2 mg, 4.0×10^{-6} mol, 0.4 mol-% per thiophene moiety) was added. The initially dark purple solution was stirred for a few minutes until a dark orange color was observed. This was followed by the addition of the thienyl halide (1.00 mmol). $HSi(OMe)_3$ (1.50 equiv., 183 mg, 191 µL per thiophene moiety) and finally dry DIPEA (3.00 equiv., 388 mg, 510 µL per thiophene moiety) were added by syringe. The reaction was stirred at 80 °C for 30 min or 60 °C for 2 h, after which all of the starting material had dissolved, forming a dark yet strongly fluorescent solution. DMF and other volatile compounds were then evaporated in vacuo whilst maintaining the reaction temperature. The solid residue was extracted with dry toluene (10–15 mL), leaving behind a colorless precipitate of the formed ammonium salts. The mixture was then stirred with small amounts of sodium sulfate for 15 min and filtered into another Schlenk flask. The filter cake was subsequently rinsed with toluene (3 × 5 mL). Evaporation of the solvent gave the products as oily waxes or amorphous solids in >90% purity, as determined by ^{1}H NMR spectroscopy. *The products should be stored at 4 °C under inert atmosphere and be used within a short time.*

Supporting Information (see footnote on the first page of this article): Synthesis of the compounds, spectroscopic data summary, copies of the NMR and IR spectra for all compounds.

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