

It was assumed that the lithiation occurs at position 2 of the thiophene ring, but the ultimate confirmation had to wait an X-ray diffraction analysis, which is reported here. The title compound **1** is stable and it was stored for 48 years, without any precautions, in contact with open air.

The X-ray diffraction analysis established the molecular structure of the title compound and surprisingly demonstrated the formation of a dimer through Cl...Cl halogen bond association, which is further self-assembled into an intricate supramolecular structure. This seems to add a new type of halogen-halogen bond association to the known types.³

A detailed NMR spectroscopic analysis of the title compound is also provided here and mass spectroscopy data are also given.

RESULTS AND DISCUSSION

Crystal structure determination

Single crystals of **1** were obtained by recrystallization from methanol. The crystals were mounted on MiTeGen microMounts cryoloops and data were collected on a Bruker D8 VENTURE diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a I μ S 3.0 microfocus source with multilayer optics, at low temperature (100 K). Further details on the data collection and refinement methods can be found in Table 1 and the experimental section.

Table 1

Crystal data and structure refinement for compound **1**

Compound	1
Empirical formula	C ₁₇ H ₁₃ Cl ₃ SSi
Formula weight	383.77
Crystal size /mm	0.286 x 0.0172 x 0.156
Crystal habit	colorless block
Wavelength (Å)	0.71073
Temperature (K)	100.(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	9.4682(6)
b (Å)	9.7595(7)
c (Å)	10.0348(7)
α (°)	71.604(2)
β (°)	88.666(2)
γ (°)	74.609(2)
Volume (Å ³)	846.47(10)
Z	2
Density (calculated) (g cm ⁻³)	1.506
Absorption coefficient (mm ⁻¹)	0.728
<i>F</i> (000)	392
θ range for data collections (°)	2.58–28.29
T _{max} / T _{min}	0.746 / 0.669
Reflections collected	35770
Independent reflections, <i>R</i> _{int}	4194, 0.0219
Completeness to $\theta = 28.29^\circ$	99.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4194 / 0 / 203
Goodness-of-fit on F ²	1.115
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0197
	<i>wR</i> ₂ = 0.0480
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0219
	<i>wR</i> ₂ = 0.0502
Largest diff. peak and hole, eÅ ⁻³	0.381, -0.216
CCDC No.	1959727

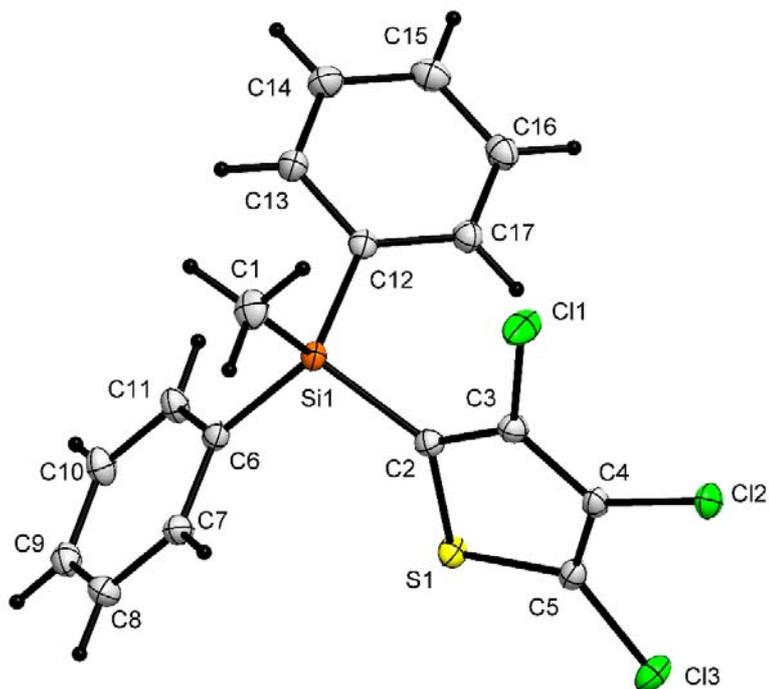


Fig. 1 – View of the asymmetric unit in the crystal of **1**, shown with 50% probability ellipsoids.

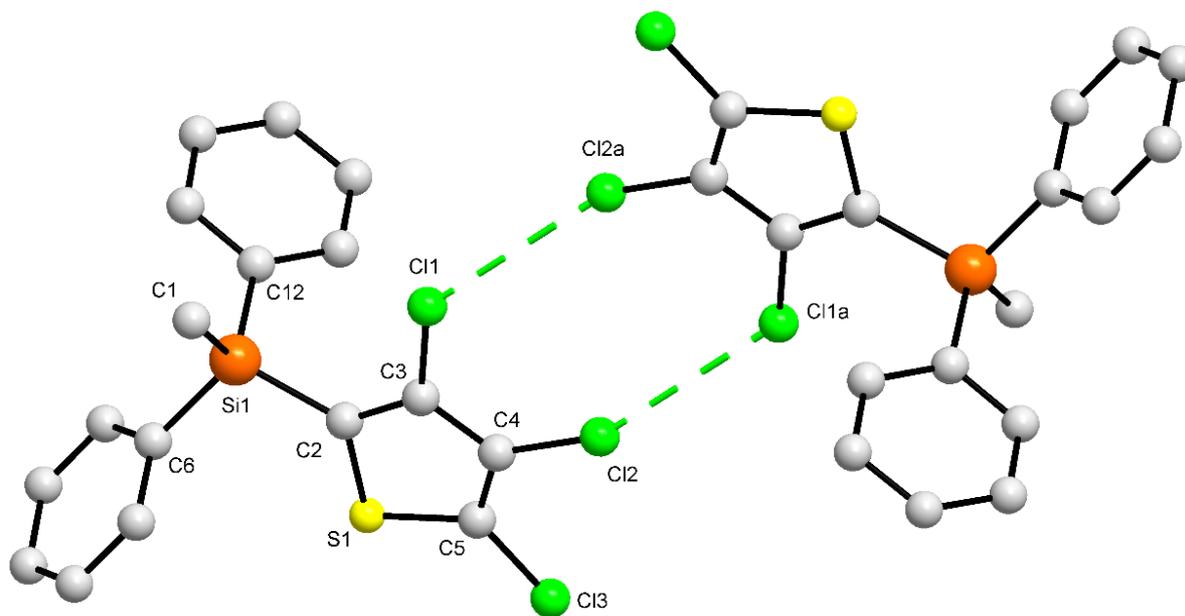


Fig. 2 – Intermolecular associations through Cl...Cl contacts in the crystal of **1** (hydrogen atoms are omitted for clarity). (Symmetry equivalent atoms are given by $-x, 1-y, -z$).

Compound **1** crystallizes in the triclinic centrosymmetric space group with two molecules in the unit cell. The X-ray diffraction revealed that the asymmetric unit consists of only one molecule (Figure 1). The geometry around the silicon atom is tetrahedral as expected, with C-Si-C angles in the range of 106.9(1)-111.5(4)° and C-Si bond lengths in the range of 1.86(1)-1.88(1) Å.

Weak Cl...Cl interactions with a *cis* arrangement lead to the formation of dimeric units (Figure 2).

In the crystal lattice further associations of the dimeric units through C-H...Cl (Figure 3), C-H... π , S... π and π ... π interactions (Figure 4) results in a tridimensional supramolecular network.⁴⁻⁷

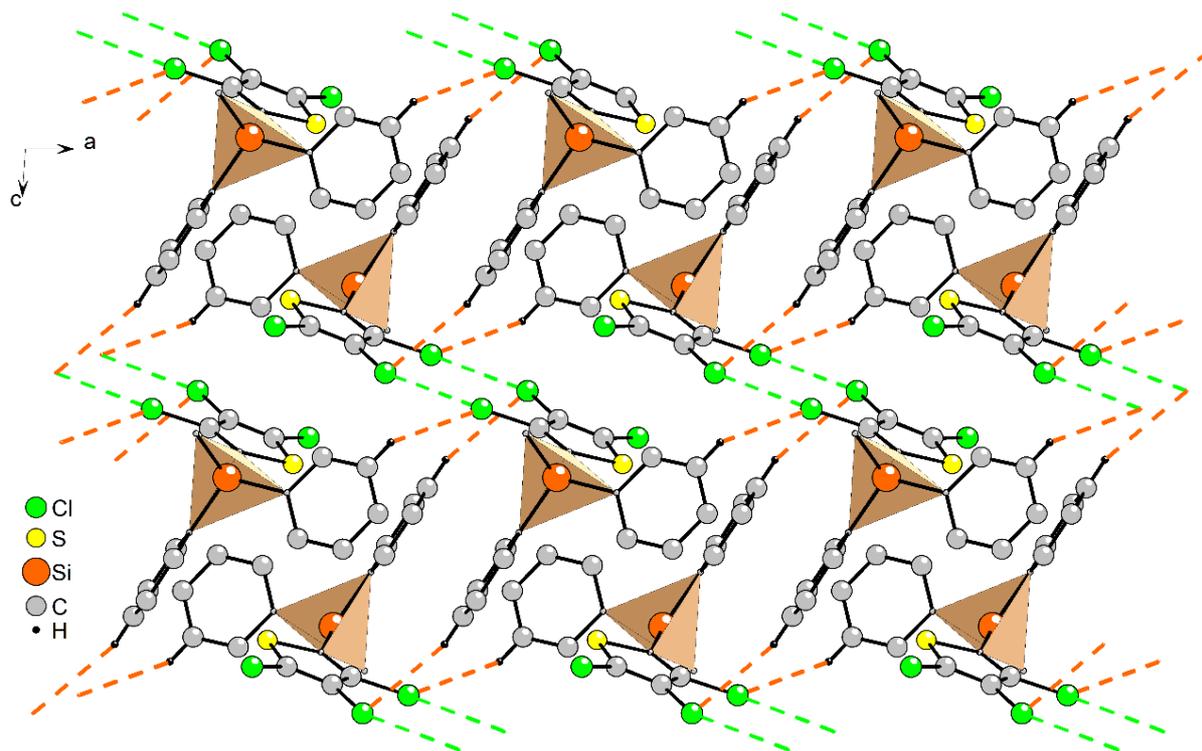


Fig. 3 – View along the *b* axis of the unit cell showing C–H...Cl contacts (orange dotted lines) and Cl...Cl contacts in the crystal of **1** (hydrogen atoms not involved in interactions are omitted for clarity).

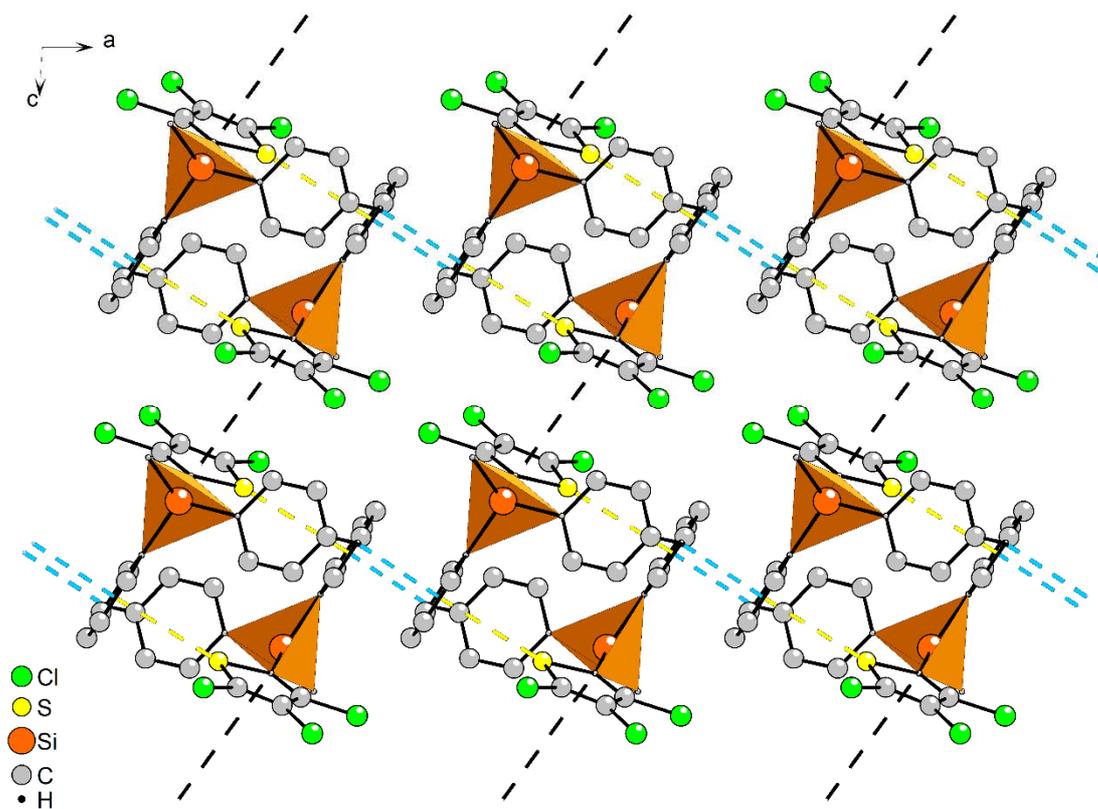
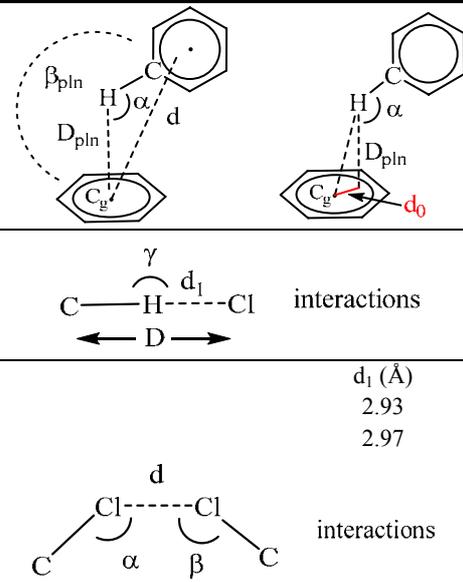


Fig. 4 – View along the *b* axis of the unit cell showing intermolecular associations through C(Ph)–H... π contacts (blue dotted lines), S... π contacts (yellow dotted lines) and π ... π contacts (black dotted lines) in the crystal of **1** (hydrogen atoms not involved in interactions are omitted for clarity).

Table 2

Intermolecular contacts for compound **1**


C-H...Cl	d_1 (Å)	γ (°)	D
C8-H8...Cl1 ^a	2.93	141.6	3.72(1)
C15-H15...Cl2 ^b	2.97	163.4	3.89(1)
C-Cl...Cl-C	d (Å)	α (°)	β (°)
C3-Cl1...Cl2 ^c -C4 ^c	3.42(1)	132.2(1)	158.2(1)
C-H... π interactions			
C-H...plane	lateral shift, d_0 (Å)	D_{pln} (Å)	α (°)
C9-H9...C(12-17) ^a	0.04	2.73	135.2(2)
π ... π interactions			
plane...plane	-	d (Å)	β_{pln} (°)
C(2-5)S1...C(2-5)S1 ^d	-	3.50	0 within s.d.
S... π interactions			
S...plane	lateral shift, d_0 (Å)	D_{pln} (Å)	β_{pln} (°)
S1...C(12-17) ^e	0.37	3.49	79.6(1)

Symmetry equivalent atoms are given by: a) 1+x, y, z b) -x, 1-y, 1-z c) -x, 1-y, -z d) 1-x, 1-y, -z e) 1-x, 1-y, 1-z

Relevant information regarding the weak intermolecular contacts is given in Table 2.

Nuclear magnetic resonance spectra

The ^1H , ^{13}C and ^{29}Si NMR spectra of compound **1** were measured in CDCl_3 solution and the numeric data are given in the experimental part.

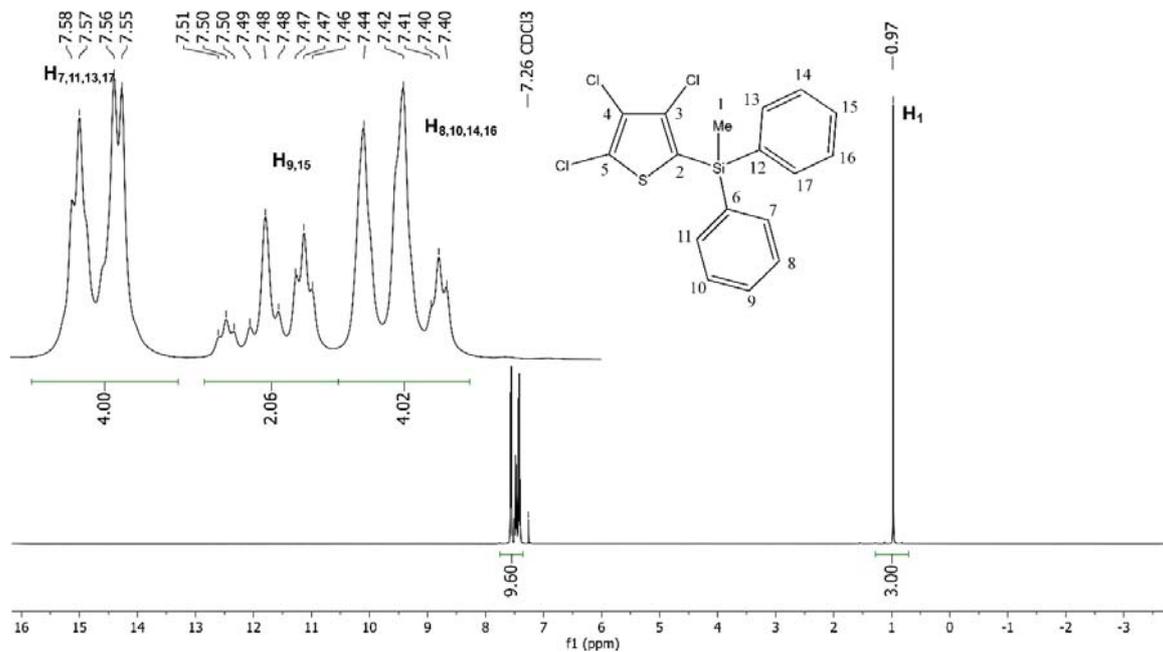
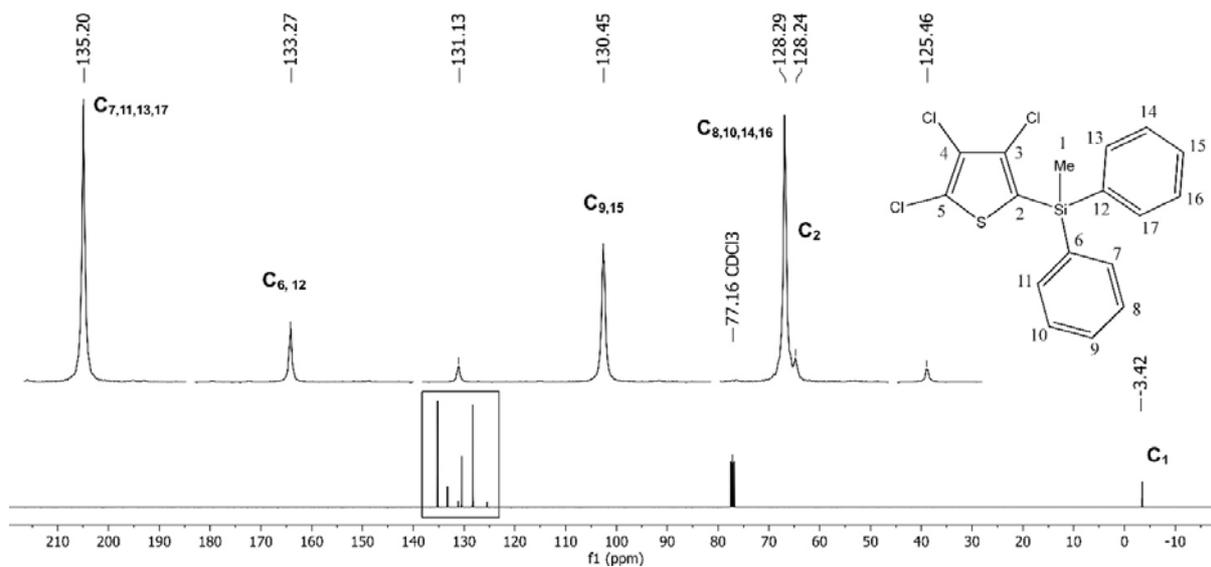
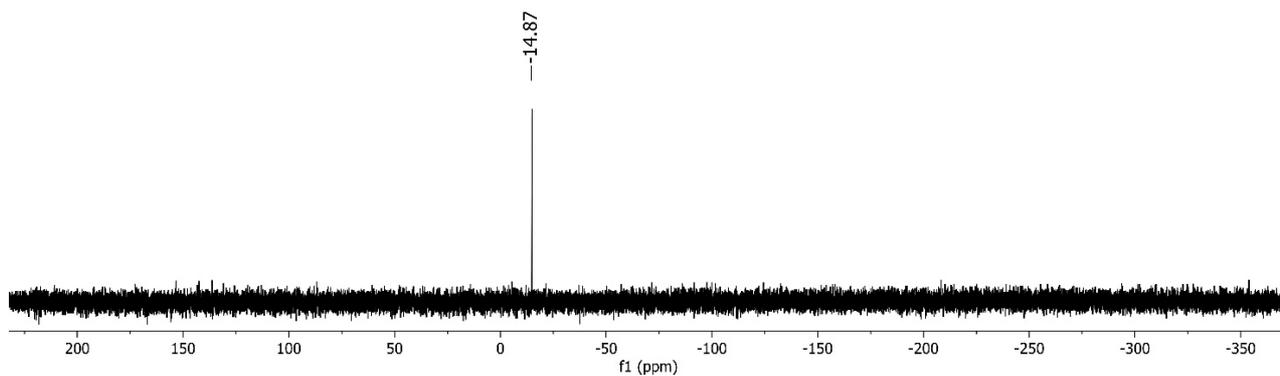
The ^1H NMR spectrum in chloroform- d_1 of the title compound shows the expected signals corresponding to the methyl and phenyl groups bonded to silicon, with an integral ratio of 3:4:4:2 for the methyl, *ortho*, *meta* and *para* hydrogen atoms respectively. Coupling between hydrogen atoms of the phenyl ring is also observed (Figure 5 and experimental data).

In the ^{13}C NMR spectrum only eight of the nine expected signals were observed, regardless of the

spectral width (Figure 6). The missing resonance signal corresponds to one of the *ipso* carbon atom bonded to chlorine from the thiophene ring. The absence of this signal could be explained by a coincidence of frequency and thus obscurement by a stronger signal.

Heteronuclear ^1H - ^{13}C (HSQC, HMBC) correlation experiments were used to establish the identity of the signals in both the ^1H and ^{13}C NMR spectra but did not help to identify the position of the missing signal nor for the correct assignment of the signals corresponding to other two *ipso* carbon atoms bonded to chlorine to the atoms. Only the *ipso* carbon atom from the thiophene ring bonded directly to silicon could be reliably attributed.

The ^{29}Si DEPT NMR spectrum shows one singlet signal as expected, at lower frequency and higher field compared to Me_4Si (Figure 7).

Fig. 5 – ¹H NMR (CDCl₃, 400.13 MHz, 21°C) spectrum of **1**.Fig. 6 – ¹³C NMR (CDCl₃, 100.61 MHz, 21°C) spectrum of **1**.Fig. 7 – ²⁹Si NMR (79.49 MHz, CDCl₃, 21°C) spectrum of **1**.

Mass spectral data

Mass spectrometry was used to investigate compound **1**. Thus, in the APCI+ spectra obtained using acetonitrile as carrying solvent, although the molecular peak was not observed several fragments resulting from the loss of organic groups Me, Ph or trichlorothieryl bonded to silicon could be identified.

EXPERIMENTAL

For structure solving and refinement of the X-ray structure the Bruker APEX3 software package was used.⁸ The structure was solved by dual methods (SHELXT-2014/5)⁹ and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-2018/3).¹⁰ The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. The drawings were created with the Diamond program.¹¹ The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The NMR spectra were recorded at room temperature on a BRUKER AVANCE 400 spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the solvent: CHCl₃ (δ 7.26 ppm) in the ¹H NMR spectrum and CDCl₃ (δ 77.16 ppm) in the ¹³C NMR spectrum, while for the ²⁹Si NMR spectrum Me₄Si was used as reference (δ 0 ppm).

The melting point was obtained using the Electrothermal 9200 digital apparatus and is uncorrected. For the mass spectrum the Thermo Scientific LTQ Orbitrap XL instrument was used.

m.p. (°C): 86.3–87.3

¹H NMR (400.13 MHz, CDCl₃) δ (ppm): 0.97 (s, 3H, Si-CH₃), 7.42 (td, 4H, *m*-C₆H₅, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1.6 Hz), 7.48 (tt, 2H, *p*-C₆H₅, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.9 Hz), 7.56 (dd, 4H, *o*-C₆H₅, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1.6 Hz).

¹³C NMR (101.61 MHz, CDCl₃) δ (ppm): -3.42 (s, Si-CH₃), 125.46 (s, *ipso*-C₄S), 128.24 (s, *ipso*-C₄S-Si), 128.29 (s, *m*-C₆H₅), 130.45 (s, *p*-C₆H₅), 131.13 (s, *ipso*-C₄S), 133.27 (s, *ipso*-C₆H₅), 135.20 (s, *o*-C₆H₅), the signal corresponding to one *ipso* carbon atom from the thiophene cycle was not observed.

²⁹Si NMR (79.49 MHz, CDCl₃) δ (ppm) -14.87 (s).

MS (APCI+, CH₃CN) *m/z* (abundance): 366.93 (100%) [M-Me]⁺, 330.96 [M-Me-Cl]⁺ (25%), 306.90 (5.1%) [M-Ph+2H]⁺ 199.06 (20.9%) [M-C₄Cl₃S+2H]⁺.

CONCLUSIONS

Halogen-metal exchange occurs in the reaction of tetrachlorothiophene with *tert*-butyllithium, leading to an organolithium derivative. Derivatization with diphenylmethylchlorosilane affords an organosilicon compound which in the solid state is associated first into halogen bond dimers, which further self-assemble into an intricate supramolecular structure, as demonstrated by single crystal X-ray diffraction.

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