

Synthesis and electrochemistry of remotely thioether-functionalized disilenes

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Dedicated to Prof. Hansgeorg Schnöckel on occasion of his 80th birthday

We report the synthesis of *p*-methylthio-functionalized disilenes with (oligo)phenylene-linkers of different sizes between the thiomethyl group and the Si=Si moiety. ²⁹Si NMR and UV/vis data suggests that the linker-size affects the Si=Si moiety only moderately. Cyclic voltammetry reveals an increasing number of reduction events with the number of phenylene rings, which are therefore clearly associated to the oligo(phenylene) linking unit. The exchange current density of the oxidation and reduction reactions as determined by linear sweep voltammetry with a rotating disc electrode also shows significant differences between the prepared disilenes.

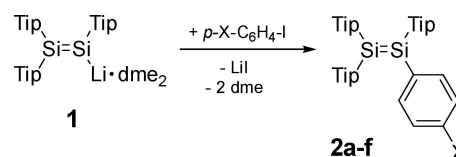
Introduction

Stable species with Si=Si double bond (disilenes) have been attracting considerable attention^[1] since their discovery in 1981 by West, Michl and Fink.^[2] The small HOMO-LUMO gap and the conformational flexibility compared to the corresponding species with C=C bonds, the alkenes, suggests significant potential for applications in organic electronics. An air-stable disilene was used as electroluminescent material in a prototypical OLED by the Tamao group.^[3] Disilenes are powerful

nucleophilic reagents for the transfer of the Si=Si moiety to various organic and inorganic substrates.^[4] The thus facile extension of π -conjugated organic substrates with Si=Si moieties allowed for the synthesis of *meta*- and *para*-phenylene-bridged tetrasiladienes^[5] as well as disilenes with residual functional groups in peripheral position (Scheme 1).^[6] The protocol also provided access to various luminescent arylene-bridged tetrasiladienes with emissions up to the near-IR at room temperature.^[7]

Given the well-established affinity of sulfur-containing groups to gold surfaces,^[8] we sought to synthesize disilenes with such groups in the remote periphery of the organic substituents in order to allow for the grafting to gold substrates. Although thiols are the most frequently applied anchor groups, we chose the much less common methyl thioether functionality SMe.^[9] Nuckolls et al. had established an appreciable conductivity even of saturated oligosilanes through break-junctions established between methyl thioethers and the gold tip of a scanning tunneling microscope.^[10] SMe groups should be inert towards intermolecular addition to Si=Si moieties, while we assumed that SH bonds would likely be prone to such undesired reactions given the well-known propensity of disilenes for 1,2-addition reactions.^[11,11]

Oligo-*para*-phenylenes of different chain length were selected as linking units of variable length because of the well-established procedures for the synthesis of α -bromo- ω -methyl thioethers as precursors, which were then going to be subjected to the standard protocol of Si=Si substitution at the bromo functionality.^[5–7] Herein, we give a preliminary report on the straightforward preparation of the targeted methylthio-functionalized (oligo)phenylene disilenes and the evaluation of their spectroscopic and electrochemical properties.



Scheme 1. Established procedure for the synthesis of *para*-functionalized phenylene-substituted disilenes **2 a–f** (Tip = 2,4,6-*Pr*₃C₆H₂, dme = 1,2-dimethoxyethane; **2 a**: X = H, **2 b**: X = F, **2 c**: X = Cl, **2 d**: X = Br, **2 e**: X = I, **2 f**: X = SiMe₃).^[5,6]

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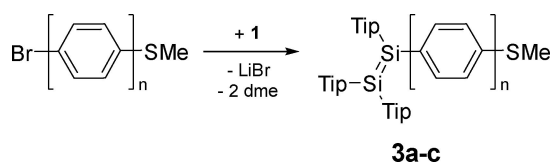
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Results and Discussion

Synthesis and spectroscopic characterization of disilenes.

Treatment of lithium disilene **1** with one equivalent of *para*-bromoaryl methyl sulfides in toluene affords the corresponding disilenes. After hexane extraction and filtration, **3a–c** are obtained as orange to red powders of NMR spectroscopic purity in very good yields (Scheme 2; **3a**: 83%, **3b**: 83%, **3c**: 78%).

Single crystals of **3a** suitable for X-ray diffraction were obtained from a concentrated pentane solution (Figure 1). The molecular structure in the solid state confirms the constitution of **3a** as the anticipated *para*-methylthiophenyldisilene. The Si1=Si2 bond length of 215.65(4) pm is in the typical range for tetraaryl-substituted disilenes and slightly shorter than in the phenyl-substituted derivative **2a** (217.5 pm). Accordingly, the *trans*-bent angles in **3a** ($\theta_{\text{Si1}}=12.09(5)^\circ$, $\theta_{\text{Si2}}=16.18(4)^\circ$) are smaller than those of **2a** ($\theta_{\text{Si1}}=23.6^\circ$, $\theta_{\text{Si2}}=22.3^\circ$), while only a minimal twisting of Si=Si bond ($\tau=4.21(5)^\circ$) is observed. The distances between the silicon atoms and the *ipso*-C atoms of the Tip groups are in a typical range (Si2–C23 188.9(1) pm, Si2–C38 188.7(1) pm, Si1–C8 188.0(1) pm), but the Si1–C1 bond length is shortened (186.4(1) pm) in comparison to the corresponding distance in **2a** (187.3 pm^[5]) suggesting a certain



Scheme 2. Synthesis of *para*-methylthio oligophenylene-substituted disilenes **3a–c** with varying number of phenylene units *n* (Tip = 2,4,6-*Pr*₃C₆H₂, dme = 1,2-dimethoxyethane; **3a**: *n* = 1, **3b**: *n* = 2, **3c**: *n* = 3).

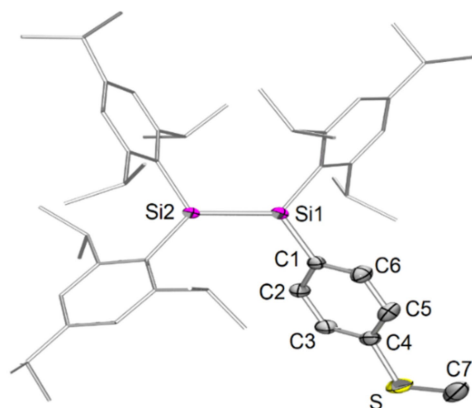


Figure 1. Molecular structure of **3a** in the solid state. Selected bond lengths [pm] and angles [°]: Si1–Si2 215.63(4); Si1–C1 186.37(11); C1–C2 140.35(16); C2–C3 138.59(17); C3–C4 139.01(19); C4–C5 139.19(19); C5–C6 139.79(18); C1–C6 139.07(17); S–C4 176.17(12); S–C7 178.2(2); Si2–Si1–C1 119.53(4); C2–C1–C6 116.93(10); C2–C3–C4 120.39(11); C4–S–C7 103.36(8); Si2–Si1–C1–C2 49.110(114).

degree of π -donation from the *para*-thiomethyl group into a σ^* -orbital at Si1 mediated by the phenylene linker. Indeed, the slightly alternating C–C bond lengths imply a quinoid structure of the phenylene unit, in line with the torsion angle of $49.1(1)^\circ$ allowing for sufficient overlap of the involved orbitals. The S–C4 distance of 176.16(12) pm is comparable to the corresponding bond in Nuckolls bis(4-(methylthio)phenyl)disilenes (175.9 pm).^[10] The S–C7 bond is only slightly shortened (178.2(2) pm vs. 179.0 pm) and the C4–S–C7 bond angle ($103.36(8)^\circ$) similarly acute (104.0°).

While no single crystals could be obtained for **3b** and **3c**, their constitution is established beyond reasonable doubt by the strong resemblance of the spectroscopic data to those of **3a**.

All thiomethyl(oligo)phenylene-substituted disilenes show two signals in ²⁹Si NMR spectra with nearly identical chemical shifts ($\delta = 55.1, 56.1$ and 56.3 ppm, $\delta = 71.2, 70.9$ and 70.8 ppm). The signals at lower field are assigned to the SiTip units and those at higher field to the for SiTip₂ fragments on the basis of HMBC ²⁹Si,¹H correlation spectra. They are almost identical to the chemical shifts reported for the phenyldisilene **2a** (55.2 and 71.2 ppm)^[5] suggesting only a minimal influence of the *para*-substituent if any, fully in line with observations for disilenes **2a–f**. ¹H and ¹³C-NMR spectra show the expected signals for three chemically inequivalent Tip groups as well as those attributed to the methylthio(oligo)phenylene linker.

UV/vis spectroscopy reveals two bands for each of the disilenes **3a–c**. The UV absorption of **3a** at $\lambda_{\text{max}}=278$ nm is assigned to the *para*-phenylene linker as it is considerably red-shifted upon extension to biphenylene (**3b**: $\lambda_{\text{max}}=295$ nm) and terphenylene (**3c**: $\lambda_{\text{max}}=303$ nm) with concomitantly increasing extinction coefficient (Table 1). This behavior is reminiscent of unsubstituted oligo(*para*-phenylenes).^[12] The longest wavelength absorption bands of **3a–c** are (as usual for disilenes) assigned to the π - π^* transitions of the Si=Si double bonds. Comparison of **3a** with **2a** reveals a small but significant red-shift of $\Delta\lambda=8$ nm with a somewhat lower absorption coefficient in case of **3a**. Upon extension of the linker to two phenylene units, a further red-shift by $\Delta\lambda=9$ nm occurs while ϵ decreases. The introduction of the third phenylene unit does not affect the longest wavelength absorption suggesting that the effective conjugation path length is already surpassed in terphenylene-substituted **3c**.

Electrochemical characterization. In order to understand the electrochemical properties of the peripherally thiofunctionalized disilenes, cyclic voltammetry (CV) experiments were

Table 1. NMR and UV/vis spectroscopic data of differently substituted disilenes.

| | 3a | 3b | 3c | 2a ^[5] |
|--|-----------|-----------|-----------|--------------------------|
| $\delta^{29}\text{Si}$ (ppm) | 55.1 | 56.1 | 56.3 | 55.2 |
| $\delta^{29}\text{Si}$ (ppm) | 71.2 | 70.9 | 70.8 | 71.8 |
| λ_1 (nm) | 278 | 295 | 303 | – |
| ϵ_1 ($10^3 \text{ M}^{-1}\text{cm}^{-1}$) | 17.8 | 27.0 | 33.9 | – |
| λ_2 (nm) | 447 | 456 | 456 | 439 |
| ϵ_2 ($10^3 \text{ M}^{-1}\text{cm}^{-1}$) | 14.8 | 10.6 | 5.0 | 19 |

performed (Figure 2). All examined disilenes show irreversible oxidation (**3a**: $E_p = +0.30$ V; **3b**: $E_p = +0.22$ V; **3c**: $E_p = +0.47$ V), which is slightly lower than in previously reported tetraaryldisilenes (e.g. $\text{Tip}_2\text{Si}=\text{SiTip}_2$; $E_{\text{ox}} = +0.56$ V, +1.32).^[13] Interestingly, **3b** seems to be most readily oxidized while **3c** required the highest potential for oxidation. In agreement with the UV-vis data, the oxidation tendency of the Si=Si moiety (**3b** > **3a** > **3c**) does not seem to correlate with the linker-size. All disilenes exhibit an additional, weaker oxidation event around +0.5 V, which is likely caused by oxidation of the thioether functionality.^[14] **3a** shows a quasi-reversible redox event at $E_{1/2} = -2.13$ V and an irreversible reduction at -2.94 V, which is accompanied by solvent decomposition. The quasi-reversible redox-event is remarkable, since this wave does not have a representation in the cyclic voltammograms of previously reported tetraaryldisilenes nor in the one of thioanisole.^[13] In comparison, the reduction of **3b** yields a comparable redox wave at -2.15 V with only marginal reoxidation. Additionally, a further irreversible reduction occurs at -2.64 V. Finally, in case of **3c**, reductions at -2.16 , -2.38 and -2.58 V are observed.

The electrochemical behavior of **3a–c** is very similar in the range of -1.0 V to $+0.5$ V, which implies a similar redox property of the Si=Si oxidation, independently of the linker size. In the more negative region, additional reductive and oxidative peaks arise. These are also assigned to reductions at the phenylene systems, which means that the larger linkers are

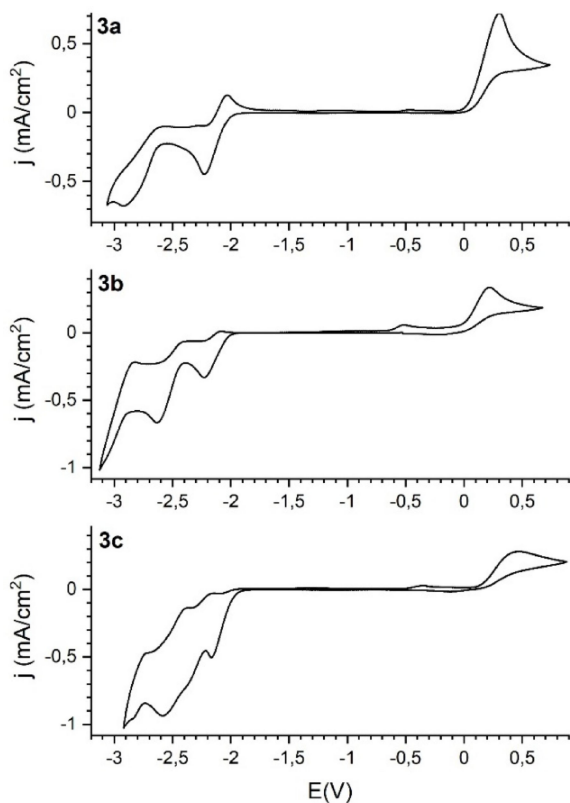


Figure 2. Cyclic voltammograms of **3a–c** (3 mM in thf with 0.1 M TBA PF₆). The Fc/Fc⁺ couple served as external reference and was fixed to +0.61 V.

available for multiple reductions. This can be also observed for *p*-biphenyl methyl thioether. With growing π -system, multiple reductions occur at more positive potentials, which is a well-established phenomenon.^[15] Accordingly, the formation of a dianion (second reduction peak) appears at the most oxidative conditions for monophenylene group in **3a** and the lowest for terphenylene group in **3c**, because of lower electron-electron repulsion. In the latter case, also a third reduction is discernable although it overlaps considerable with the preceding one at lower potential. Except for the first reduction of **3a**, the corresponding oxidative events are hardly observed at all. This irreversibility indicates decomposition of the produced anions at the applied scan rate.

In order to gather preliminary results on the electron transfer process between electrode and analyte, linear sweep voltammetry with a rotating disc electrode (RDE) and a sweep velocity of 50 mV/s was performed on disilenes **3a–c**. Using a Tafel plot, the exchange current density j_0 as a measure for electrochemical activity on the electrodes is graphically accessible by plotting E vs. $\log(j)$ for the kinetically limited area.

$$E = E^0 + \left(2.303 \frac{RT}{\alpha n F}\right) \log(j_0) - \left(2.303 \frac{RT}{\alpha n F}\right) \log(j)$$

Herein, the number of transferred electrons were assumed as $n = 1$ and the transfer coefficient $\alpha = 0.5$.

According to the exchange current densities of **3a–c** (Table 2), the rate of the oxidation reaction is by two orders of magnitude higher than that of the reduction. There is no discernable trend regarding the effect of the linker size on the exchange current density: terphenylene compound **3c** shows the highest redox activity, followed by the phenylene compound **3a**.

In conclusion, stable disilenes with remote thioether functionality are accessible from a lithium disilene using the standard protocol of a formal nucleophilic aromatic substitution with aryl bromide substrates. While the length of the linking unit does indeed have an influence on the number of reduction events of these disilenes, the separation of the different waves is not very much pronounced adversely affecting the reversibility at the applied scan rate.

Table 2. Electrochemical data from linear sweep voltammetry with rotating disc electrode (RDE).^[a]

| Compound | E^0 (V) vs. NHE | | j_0 @ 500 min ⁻¹ (mA/cm ²) | |
|-----------|-------------------|-----------|---|----------------------|
| | Oxidation | Reduction | Oxidation | Reduction |
| 3a | -0.418 | -2.055 | 1.1×10^{-3} | 7.8×10^{-5} |
| 3b | -0.444 | -2.063 | 4.5×10^{-4} | 7.4×10^{-6} |
| 3c | -0.429 | -2.054 | 2.5×10^{-2} | 7.0×10^{-4} |

[a] Experiments were carried out under an inert atmosphere of argon in thf with TBA PF₆ as supporting electrolyte. A Pt RDE working electrode ($d = 3$ mm) and an Ag quasi-reference electrode with Fc/Fc⁺ as reference were used.

Experimental Section

All reactions were carried out in a protective argon atmosphere using classical Schlenk techniques or gloveboxes. Pentane was refluxed with sodium/benzophenone and distilled prior to use. Hexane, tetrahydrofuran and toluene were taken directly from a solvent purification system (Innovative Technology PureSolv MD7). C_6D_6 was refluxed over potassium and distilled prior to use. NMR data were recorded at 300 K on a Bruker Avance III 300 (1H : 300.13 MHz, ^{13}C : 75.47 MHz, ^{29}Si : 59.6 MHz). The residual protons of the deuterated solvents serve as a reference in 1H NMR spectra. The solvent itself serves as reference for ^{13}C NMR; ^{29}Si was referenced to external $SiMe_4$ standard. UV/vis spectra were acquired with a Perkin Elmer Lambda 35 spectrometer using quartz cells with a path length of 0.1 cm. Melting points were determined under argon in sealed NMR tube and are uncorrected. Elemental analysis was carried out with an elemental analyzer Leco CHN-900. 4-Bromothioanisole (97%), 1-bromo-4-iodobenzene (98%), magnesium turnings, tetrakis(triphenylphosphine)palladium(0) (99%) were purchased from Sigma Aldrich. 4-Bromo-4'-iodobiphenyl was purchased from Alfa Aesar. All commercially obtained starting materials were used as supplied without further purification. Disilene **1**^[6] and 1-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)disilene **2a**^[5] were prepared according to literature. 4'-Bromo-4-methylthio-bi- and terphenyl were prepared as described below according to a slightly modified literature procedure.^[9c]

Synthesis of 4'-bromo-4-methylthiobiphenyl. Magnesium turnings (1.3 g, 52.5 mmol) were heated in vacuum and afterwards suspended in a solution of 4-bromothioanisole (10.0 g, 49.3 mmol) in 70 mL of thf. The suspension was stirred for 2 hours causing gentle reflux. 1-Bromo-4-iodobenzene (14.0 g, 49.4 mmol) and $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol) were dissolved in 40 mL of thf and heated to reflux. The resulting solution of 4-Bromophenylmagnesium iodide was added dropwise within 30 min and refluxed for additional 2 hours. Afterwards the reaction mixture was poured into an ice-cold solution of 5% HCl. The resulting white solid was filtered and dried in vacuo. The crude product was crystallized from 1:1 isopropanol/n-heptane twice to obtain 9.6 g (34.4 mmol, 70%) of 4'-Bromo-4-methylthiobiphenyl. 1H -NMR (400 MHz, $CDCl_3$, 300 K, TMS): δ = 2.52 (s, 3H, SCH_3), 7.32 (d, 3J = 8.58 Hz, 2H), 7.43 (d, 3J = 8.64 Hz, 2H), 7.48 (d, 3J = 8.61 Hz, 2H), 7.55 ppm (d, 3J = 8.64 Hz, 2H); ^{13}C -NMR (75.5 MHz, $CDCl_3$, 300 K, TMS): δ = 15.9 (SCH_3), 121.5 ($PhC-Br$), 127.4, 128.5, 128.6, 132.0, 132.2 (all $PhC-H$), 138.8, 138.4 (both $PhC-CPh$), 140.0 ppm ($PhC-S$).

Synthesis of 4-bromo-4''-methylthio-p-terphenyl. Magnesium turnings (114 mg, 4.75 mmol) were heated in vacuum and afterwards suspended in a solution of 4-bromothioanisole (0.96 g, 4.74 mmol) in 40 mL of thf. The suspension was stirred for 2 hours causing gentle reflux. 4-Bromo-4'-iodobiphenyl (1.72 g, 4.80 mmol) and $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol) were dissolved in 100 mL of thf and heated to reflux. The resulting solution of 4-Bromobiphenyl-4'-magnesium iodide was added dropwise within 30 min and refluxed for additional 2 hours. All volatile components were removed in vacuo. The resulting yellow solid was dissolved in approx. 300 mL of boiling toluene and filtered while still hot. The solution was stored at $-8^\circ C$ overnight. 4-Bromo-4''-methylthio-p-terphenyl was obtained as an off-white powder (0.85 g, 2.38 mmol). The mother liquor was concentrated under reduced pressure yielding a second fraction (0.23 g, 0.66 mmol, total yield: 64.2%). 1H -NMR (400 MHz, $CDCl_3$, 300 K, TMS): δ = 2.54 (s, 3H, SCH_3), 7.35 (d, 3J = 8.52 Hz, 2H), 7.50 (d, 3J = 8.67 Hz, 2H), 7.55–7.60 (m, 4H), 7.64 ppm (d, 3J = 2.64, 4H). Due to the poor solubility of the compound, no ^{13}C -NMR spectrum is available.

General protocol for the synthesis for ω -methylthio oligophenylene disilenes **3a–c.** A suspension of the appropriate ω -thiomethyl

(oligo)phenylene bromide (0.58 mmol) in 20 mL toluene was cooled to $-80^\circ C$. A solution of 505 mg lithium disilene **1** (0.52 mmol) in 20 mL toluene was added by cannula and the resulting mixture was allowed to slowly warm up to room temperature overnight. The solvent was removed *in vacuo* and the resulting red-orange solid was extracted with 30 mL n-hexane, in case of **3c** with 60 mL of warm n-hexane. The extract was reduced to dryness.

1-(4-(Methylthio)phenyl)-1,2,2-tris(2,4,6-triisopropylphenyl)

disilene 3a. Product was isolated in 83% yield (356 mg, 0.43 mmol) as an orange powder. Single crystals suitable for XRD were grown from n-pentane at room temperature. M.p.: $112^\circ C$, 1H -NMR (400 MHz, C_6D_6 , 300 K, TMS): δ = 1.08, 1.14, 1.19, 1.20, 1.24 (all d, all together 54 H, $CH(CH_3)_2$ of Tip), 1.84 (s, 3 H, SCH_3), 2.71, 2.77 (both sept, all together 3 H, para $CH(CH_3)_2$ of Tip), 4.23 (sept, 2 H, ortho $CH(CH_3)_2$ of Tip), 4.24, 4.31 (both sept, all together 4 H, ortho $CH(CH_3)_2$ of Tip), 6.76 (d, 2 H, H of methylthiophenyl), 7.06, 7.11, 7.15 (all s, 1H each, meta TipH), 7.25 ppm (d, 2 H, H of methylthiophenyl); ^{13}C -NMR (75.5 MHz, C_6D_6 , 300 K, TMS): δ = 14.7 (SCH_3), 24.0, 24.2, 24.4, 24.7, 25.8 (iPr- CH_3), 34.6, 34.7, 34.9, 37.6, 38.2, 38.4 (iPr-CH), 121.7, 122.1 (Tip m-C), 125.7 (phenylene CH), 130.5, 133.2, 133.5, 134.3 (Tip/phenylene CSi), 136.5 (phenylene CH, SCH_3 side), 140.1 ($CSCH_3$), 150.7, 151.4, 151.8, 155.1, 155.8, 156.3 (Tip, o,p-C); ^{29}Si -NMR (59.6 MHz, C_6D_6 , 300 K, TMS): δ = 55.1, 71.2 ppm; UV/vis (n-hexane): λ_{max} (ϵ) = 447 nm ($14800 M^{-1}cm^{-1}$), 278 nm ($17800 M^{-1}cm^{-1}$); Elemental analysis calculated for $C_{52}H_{76}SSi_2$: C, 79.12; H, 9.70; S, 4.06; Found: C, 76.97; H, 9.54; S 3.30.

1-(4'-(Methylthio)-[1,1'-biphenyl]-4-yl)-1,2,2-tris(2,4,6-triisopropylphenyl)disilene.

Product was isolated in 83% yield (356 mg, 0.43 mmol) as a red powder. M.p.: $87^\circ C$; 1H -NMR (400 MHz, C_6D_6 , 300 K, TMS): δ = 7.28 (d, 2H, phenylene-H), 7.28–6.99 (m, 12H, phenylene-H and Tip-H), 4.45–4.20 (m, 3H, iPr-CH), 4.19–3.95 (m, 2H, iPr-CH), 2.88–2.59 (m, 4H, iPr-CH), 1.99 (s, 3H, SCH_3), 1.29–1.03 (m, 54H, iPr- CH_3); ^{13}C -NMR (75.5 MHz, C_6D_6 , 300 K, TMS): δ = 15.8 (SCH_3), 24.3, 24.5, 24.7, 25.0, 26.1 (iPr- CH_3), 34.9, 35.1, 35.3, 38.0, 38.6, 38.8 (iPr-CH), 122.1, 122.5 (Tip, m-C), 126.6, 127.6, 127.8 (biphenyl CH), 128.9 (Tip, m-C), 130.8, 133.6, 133.8 (Tip/biphenyl CSi), 137.1 (biphenyl CH, SCH_3 side), 137.9, 138.1, 138.6 (Tip CSi or biphenyl), 140.9 (biphenyl $CSCH_3$), 151.1, 151.8, 152.2 (Tip, o,p-C), 155.5, 156.1, 156.7 (Tip, o,p-C); ^{29}Si -NMR (59.6 MHz, C_6D_6 , 300 K, TMS): δ = 70.85 (s), 56.10 (s) ppm; UV/vis (n-hexane): λ_{max} (ϵ) = 456 nm ($10600 M^{-1}cm^{-1}$), 295 nm ($27000 M^{-1}cm^{-1}$); Elemental analysis calculated for $C_{58}H_{80}SSi_2$: C, 80.49; H, 9.32; Found: C, 79.70; H, 9.26.

1-(4''-(Methylthio)-[1,1':4',1''-terphenyl]-4-yl)-1,2,2-tris(2,4,6-triisopropylphenyl)disilene.

Product was isolated in 78% yield (434 mg, 0.46 mmol) as a red powder. M.p.: $99^\circ C$; 1H -NMR (400 MHz, C_6D_6 , 300 K, TMS): δ = 7.74–6.57 (m, 24H, terphenylene-H and Tip-H), 4.52–2.47 (m, 9H, iPr-CH), 2.09 (s, 3H, SCH_3), 1.79–0.20 (m, 54H, iPr- CH_3); ^{13}C -NMR (75.5 MHz, C_6D_6 , 300 K, TMS): δ = 15.8 (SCH_3), 24.3, 24.5, 24.7, 25.0, 26.1 (iPr- CH_3), 34.9, 35.1, 35.3, 37.9, 38.6, 38.8 (iPr-CH), 122.1, 122.5 (Tip, m-C), 126.8, 127.6, 127.7, 127.8, 128.0 (terphenyl CH), 128.6 (Tip, m-C), 130.8, 133.6, 133.8 (Tip/terphenyl CSi), 137.1 (terphenyl CH, SCH_3 side), 138.2, 138.3, 138.8, 140.2, 140.3, 141.0 (Tip/terphenyl CSi or terphenyl), 151.2, 151.8, 152.2, 155.5, 156.2, 156.7 (Tip, o,p-C); ^{29}Si -NMR (59.6 MHz, C_6D_6 , 300 K, TMS): δ = 70.76 (s), 56.26 (s); UV/vis (n-hexane): λ_{max} (ϵ) = 456 nm ($5000 M^{-1}cm^{-1}$), 303 nm ($33900 M^{-1}cm^{-1}$). Elemental analysis calculated for $C_{64}H_{84}SSi_2$: C, 81.64; H, 8.99; Found: C, 79.26; H, 9.02.

Electrochemical characterization. Cyclic and linear sweep voltammetry were carried out with a Metrohm Autolab PGStat101 potentiostat in a typical three electrode setup in a glovebox at room temperature. All measurements were done with a thf solution of 3 mM analyte and 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. A silver rod was used as quasi-reference electrode. However, potentials in this study are referenced to the

ferrocene/ferrocenium couple whose potential was fixed to +0.61 V in THF. Counter electrode was a platinum wire. In cyclic voltammetry, a freshly polished platinum electrode ($A = 0.0314 \text{ cm}^2$) served as working electrode. The cycles were repeated several times at a scan rate of 100 mVs^{-1} . The first cycle was used for discussion. In linear sweep voltammetry, a platinum RDE working electrode with a diameter of 3 mm was used at a scan rate of 50 mVs^{-1} .

Crystallography. The data set was collected using a Bruker X8 Apex diffractometer. Graphite-monochromated $\text{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used. Data on a single crystal of **3a** were collected at 172(2) K and corrected for absorption effects using the multi-scan method. The structure was solved by direct methods using SHELXS-97^[17] and was refined by full matrix least squares calculations on F2 (SHELXL2018^[18]) in the graphical user interface Shelxle.^[19] All non H-atoms were located on the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH_2) or 1.5 (CH_3). Disorder: One n-pentane solvent molecule was disordered over a center of inversion. Its occupancy factors were set to 0.5 and some restraints were applied to the anisotropic displacement parameters of the disordered atoms. Details of the crystal structure of **3a** have been deposited with the Cambridge Structural Data Center as CCDC-2081035.

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