Supporting Information

Azaacene Dimers: Acceptor Materials with a Twist

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S1. General Remarks

Reagents and solvents for synthesis
All reagents were obtained from commercial suppliers and were used without further purification. Deuterated solvents were purchased from Sigma-Aldrich Laborchemikalien GmbH (Seelze, Germany). All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen free nitrogen or argon atmosphere using Schlenk and glovebox techniques.

Column chromatography
Column chromatography was performed using silica gel from Macherey, Nagel & Co. KG (Düren, Germany) (particle size: 0.040 - 0.063 mm). For TLC Polygram Sil G/UV 254 plates from Macherey, Nagel & Co. KG (Düren, Germany) were used and examined under UV-light irradiation (254 nm and 365 nm). Before column chromatography the crude product was mixed with Celite 545 and DCM to make a slurry. The solvent was removed by rotary evaporation to get a dry powder.

Gel permeation chromatography
Preparative GPC was performed on Bio-Beads® (S-X1 Beads, 200 – 400 Mesh, crosslinked polystyrene), purchased from Bio-Rad Laboratories, Inc., using toluene as solvent.

$^1$H NMR spectra and $^{13}$C NMR spectra
All spectra were recorded at room temperature on a Bruker Avance III 600 ($^1$H: 600 MHz, $^{13}$C: 151 MHz), Bruker Avance III 500 ($^1$H: 500 MHz, $^{13}$C: 126 MHz) or Bruker Avance III 300 ($^1$H: 301 MHz). $^{13}$C NMR spectra were measured proton decoupled if not stated otherwise. NMR spectra were integrated and processed using the Software TopSpin 3.5pl5 (Bruker). For calibration the residual solvent peaks were referenced.[1] Chemical shifts $\delta$ are reported in ppm and coupling constants $J$ in Hz. The following abbreviations describe the observed multiplicities: $s$ = singlet, $d$ = doublet, $m$ = multiplet.

IR spectra
All spectra were recorded neat at room temperature on a Jasco FT/IR-4100. Signals are reported in wavenumbers [cm$^{-1}$].
**Mass spectrometry**
The mass spectra were recorded using the following instruments: Bruker ApexQe hybrid 9.4 T FT-ICR (MALDI); Bruker AutoFlex Speed time-of-flight (MALDI).

**Melting points**
Melting points were determined in open glass capillaries with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK).

**Cyclic voltammetry**
The cyclic voltammetry (CV) experiments were carried out using PGSTAT101 Potentiostat Galvanostat with a platinum working electrode (Metrohm 6.120.4190, diameter 1 mm), a platinum wire auxiliary electrode (Metrohm 3.109.0790), a silver wire reference electrode (Metrohm 6.1241.060), a 0.1 mol L⁻¹ NBu₄PF₆ solution in degassed, dry DCM, and ferrocene/ferrocenium as the reference redox system and internal standard (−5.1 eV) at room temperature and 0.2 V s⁻¹. To determine the reduction and oxidation potentials, the half-wave potentials were used.[²]

**X-ray single-crystal structure analysis**
X-ray single-crystal structure analyses were measured on a Bruker Smart APEX-II Quazar Area Detector diffractometer by Dr. F. Rominger (Heidelberg University). Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F2 with the full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL software package.

**UV-Vis and fluorescence spectroscopy**
Absorption spectra were recorded on a Jasco UV-Vis V-660 or Jasco UV-Vis V-670. Fluorescence spectra were recorded on a Jasco FP-6500.

**Quantum yields**
Quantum yields were determined by an Ulbricht sphere (6 inch) using a PTI QuantaMaster 40 equipped with a Hamamatsu R928P Photomultiplier.
Quantum lifetimes
Quantum lifetimes were determined on a Horiba FluoroCube-01-NL lifetime spectrofluorometer with emission monochromator (Seya-Namioka type, 200 nm to 800 nm) and diode excitation (Nano-LED N-375L, 375 ± 10 nm, < 200 ps).

Camera
The photos were taken by a Canon EOS 7D under daylight or UV-light irradiation (λ = 365 nm).

Computational studies
Computational studies were carried out using DFT calculations on Turbomole 6.3.1 and Gaussian16. Geometry optimizations were performed using the B3LYP functional and def2-TZVP basis set. At this geometry, the absolute energy and FMO energies were assigned by a single-point approach at the B3LYP/6-311++G** level of theory.[3]
S2. Synthesis

3,6-Bis((trisopropylsilyl)ethyl)benzene-1,2-diamine (2a),[4] 1,4-bis((trisopropylsilyl)ethyl)napthalene-2,3-diamine (2b),[5] 1,4-bis((trisopropylsilyl)ethyl)anthracene-2,3-diamine (2c),[4] 1,4-bis((trisopropylsilyl)ethyl)phenazine-2,3-diamine (2d),[6] 4,7-bis((trisopropylsilyl)ethyl)benzo[c][1,2,5]thiadazole-5,6-diamine (2e),[7] 1,4-bis((trisopropylsilyl)ethyl)phenazine (4a),[8] 6,11-bis((trisopropylsilyl)ethyl)benzo[b]phenazine (4b),[5] 6,13-bis((trisopropylsilyl)ethyl)naphtho[2,3-b]phenazine (4c)[9] and 6,13-bis((trisopropylsilyl)ethyl)quinoxalino[2,3-b]phenazine (4d)[10] were synthesized according to literature procedures.

General procedure:

In a heatgun dried Schlenk tube under an atmosphere of argon was added quinone 1 (1.00 equiv.) and the ortho-diamine 2 (2.00 equiv). Then chloroform and acetic acid were added and the reaction mixture stirred at 50 °C for 15 h. The mixture was cooled to room temperature and diluted with water (10 mL). The phases were separated, and the aqueous layer was extracted with dichloromethane (3×10 mL). The combined organic phases were washed with sodium bicarbonate solution (10 mL), dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/diethyl ether 250:1 v/v) and gel permeation chromatography (toluene) the product 3 was isolated.

3,3',3',3'-Tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[1H-indene]-5,5',6,6'-tetrone (1)

\[
\begin{align*}
\text{HO} & \quad \text{NaIO}_4 \\
\text{DCM/EtOH} & \quad \text{HO} \\
\text{HO} & \quad \text{O}
\end{align*}
\]

In a flask was dissolved racemic 3,3',3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[1H-indene]-5,5',6,6'-tetrrol (3.00 g, 8.81 mmol, 1.00 equiv.) in 40 mL ethanol and was then diluted with 150 mL dichloromethane. A solution of sodium periodate (4.15 g, 19.4 mmol, 2.20 equiv.) in 40 mL distilled water was added and the reaction mixture stirred at room temperature for 1 h. The phases were separated, and the aqueous layer was extracted with dichloromethane (3×30 mL). The combined organic phases were washed with brine (20 mL), dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the title compound 1 was isolated as a red solid (2.78 g, 8.28 mmol, 94 %).
$^1$H NMR (CDCl$_3$, 301 MHz, RT): $\delta = 6.27$ (d, $J = 0.55$ Hz, 2H), 6.17 (d, $J = 0.55$ Hz, 2H), 2.38 (d, $J = 13.5$ Hz, 2H), 2.24 (d, $J = 13.5$ Hz, 2H), 1.41 (s, 6H), 1.39 (s, 6H) ppm. All analytical data is in good agreement with literature.$^{[11]}$ Single crystalline specimen was obtained by slow diffusion of methanol into a chloroform solution of 1.

4,11-Bis(((triisopropylsilyl)ethynyl)-[1,2,5]thiadiazolo[3,4-b]phenazine (4e)

In a heatgun dried Schlenk tube under an atmosphere of argon was suspended 2d (100 mg, 175 $\mu$mol, 1.00 equiv.) in 1.5 mL anhydrous pyridine. N-thionylaniline (41.3 $\mu$L, 51.2 mg, 368 $\mu$mol, 2.10 equiv.) was added and after stirring the reaction mixture at 80 °C for 5 min, trimethylsilyl chloride (222 $\mu$L, 190 mg, 1.75 mmol, 10.0 equiv.) was slowly added to the suspension. The reaction mixture was stirred at 80 °C for 6 h. The mixture was cooled to room temperature and diluted with 10 mL DCM. The mixture was washed with 1N hydrochloric acid (2 x 10 mL) and sodium bicarbonate solution (10 mL), dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/diethylether 250:1 v/v -> 100:1 -> 50:1) and gel permeation chromatography (toluene) the product 4e was isolated as a dark blue solid (21.6 mg, 36.1 $\mu$mol, 21 %).

$^1$H NMR (CDCl$_3$, 301 MHz, RT): $\delta = 8.09$ - 8.16 (m, 2H), 7.75 - 7.82 (m, 2H), 1.30 - 1.34 (m, 42H) ppm. All analytical data is in good agreement with literature.$^{[12]}$

3,3',3'-Tetramethyl-6,6',9,9'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]phenazine] (3a)
The GP was applied to 1 (100 mg, 297 μmol, 1.00 equiv.) and 2a (279 mg, 595 μmol, 2.00 equiv.) in 1.5 mL chloroform and 1.5 mL acetic acid. Flash column chromatography (SiO₂; petroleum ether/diethyl ether 250:1 v/v) and gel permeation chromatography (toluene) yielded a yellow solid 3a (237 mg, 197 μmol, 66%).

Rₜ = 0.76 (SiO₂; petroleum ether/dichloromethane 2:1, v/v). Mp: 185 °C. ¹H NMR (CDCl₃, 600 MHz, RT): δ = 8.06 (s, 2H), 7.90 (d, J = 7.40 Hz, 2H), 7.86 (d, J = 7.40 Hz, 2H), 7.64 (s, 2H), 2.66 - 2.73 (m, 4H), 1.70 (s, 6H), 1.60 (s, 6H), 1.27 - 1.31 (m, 42H), 1.06 - 1.11 (m, 42H) ppm. ¹³C NMR (CDCl₃, 151 MHz, RT): δ = 158.2, 157.6, 143.8, 143.8, 143.0, 142.9, 133.6, 133.4, 124.9, 124.5, 124.2, 122.0, 104.1, 103.8, 100.8, 100.4, 60.3, 57.4, 44.0, 32.1, 30.6, 19.0, 18.8, 11.7, 11.5 ppm. IR (ATR): ν = 2941, 2863, 1461, 1036, 996, 880, 847, 787, 742, 764, 660, 644, 633, 581, 457 cm⁻¹. HRMS (MALDI⁺) m/z: [M⁺]: calcd. for [C₂₇H₁₀₀N₄Si₄⁺]: 1200.7646; found 1200.7693; correct isotope distribution.

3,3',3'-Tetramethyl-6,6',11,11' tetakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobenzo[b]cyclopenta[̃-phenazine] (3b)

The GP was applied to 1 (40.0 mg, 119 μmol, 1.00 equiv.) and 2b (123 mg, 238 μmol, 2.00 equiv.) in 1.0 mL chloroform and 1.0 mL acetic acid. Flash column chromatography (SiO₂; petroleum ether/diethyl ether 250:1 v/v) and gel permeation chromatography (toluene) yielded red solid 3b (133 mg, 102 μmol, 86%).

Rₜ = 0.74 (SiO₂; petroleum ether/dichloromethane 2:1, v/v). Mp: 212 °C. ¹H NMR (CDCl₃, 600 MHz, RT): δ = 8.75 (d, J = 8.08 Hz, 2H), 8.69 (d, J = 8.01 Hz, 2H), 8.06 (s, 2H), 7.68 (s, 2H), 7.59 - 7.67 (m, 4H), 2.66 - 2.80 (m, 4H), 1.74 (s, 6H), 1.64 (s, 6H), 1.33 - 1.44 (m, 42H), 1.09 - 1.21 (m, 42H) ppm. ¹³C NMR (CDCl₃, 126 MHz, RT): δ = 158.8, 158.2, 144.9, 144.8, 141.1, 140.9, 135.2, 135.0, 127.9, 127.8, 127.7, 127.7, 125.0, 122.0, 120.9, 120.5, 108.2, 107.8, 103.2, 102.9, 60.2, 57.3, 43.9, 32.0, 30.6, 19.1, 18.9, 11.8, 11.6 ppm. IR (ATR): ν = 2941, 2862, 1461, 1442, 1389, 1367, 1042, 995, 879, 759, 675, 660, 593, 482, 403 cm⁻¹. HRMS (MALDI⁺) m/z: [M⁺]: calcd. for [C₈₅H₁₁₂N₄Si₄⁺]: 1300.7959; found 1300.7983; correct isotope distribution.
3,3',3'-Tetramethyl-6,6',13,13'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]naphtho[2,3-]phenazine] (3c)

The GP was applied to 1 (85.7 mg, 255 μmol, 1.00 equiv.) and 2c (290 mg, 510 μmol, 2.00 equiv.) in 1.5 mL chloroform and 1.5 mL acetic acid. Flash column chromatography (SiO2; petroleum ether/diethyl ether 250:1 v/v) and gel permeation chromatography (toluene) yielded a green solid 3c (251 mg, 179 μmol, 70%).

Rf = 0.73 (SiO2; petroleum ether/dichloromethane 2:1, v/v). Mp: ≥400 °C. 1H NMR (CDCl3, 600 MHz, RT): δ = 9.42 (s, 2H), 9.37 (s, 2H), 8.00 (s, 2H), 7.97 - 8.03 (m, 4H), 7.64 (s, 2H), 7.43 - 8.48 (m, 4H). 13C NMR (CDCl3, 151 MHz, RT): δ = 159.1, 158.5, 145.3, 145.3, 140.9, 140.7, 133.0, 132.9, 132.7, 132.6, 128.8, 128.8, 127.0, 126.8, 126.8, 126.7, 125.2, 122.1, 120.8, 120.3, 109.6, 109.1, 104.2, 103.8, 60.1, 57.3, 44.0, 32.0, 30.5, 19.2, 19.0, 11.9, 11.7 ppm. IR (ATR): ν = 2940, 2862, 1460, 1375, 1139, 1016, 994, 751, 740, 668, 651, 578, 462, 418 cm⁻¹. HRMS (MALDI+) m/z: [M]+: calcd. for [C93H116N4Si4]⁺: 1400.8272; found 1400.8243; correct isotope distribution.

3,3',3'-Tetramethyl-6,6',13,13'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]quinoxalino[2,3-]phenazine] (3d)

The GP was applied to 1 (100 mg, 297 μmol, 1.00 equiv.) and 2d (279 mg, 5.95 μmol, 2.00 equiv.) in 1.5 mL chloroform and 1.5 mL acetic acid. Flash column chromatography (SiO2; petroleum ether/diethyl ether 250:1 v/v -> 100:1 -> 50:1) and gel permeation chromatography (toluene) yielded green solid 3d (277 mg, 197 μmol, 66%).
Rf = 0.40 (SiO2; petroleum ether/dichloromethane 2:1, v/v). Mp: ≥400 °C. 1H NMR (CDCl3, 500 MHz, RT): δ = 8.16 - 8.24 (m, 4H), 8.07 (s, 2H), 7.77 - 7.84 (m, 4H), 7.70 (s, 2H), 2.70 - 2.80 (m, 4H), 1.76 (s, 6H), 1.66 (s, 6H), 1.39 - 1.44 (m, 42H), 1.17 - 1.25 (m, 42H) ppm. 13C NMR (CDCl3, 126 MHz, RT): δ = 160.1, 159.4, 145.8, 145.8, 145.5, 145.5, 143.0, 142.9, 142.7, 142.5, 132.0, 132.0, 130.7, 130.6, 125.3, 122.9, 122.5, 122.4, 112.7, 112.1, 103.4, 103.1, 60.0, 57.5, 44.1, 32.0, 30.5, 19.2, 19.0, 11.9, 11.7 ppm. IR (ATR): ν̃ = 2940, 2862, 1452, 1429, 1382, 1311, 1117, 1023, 966, 881, 734, 582, 419 cm⁻¹. HRMS (MALDI⁺) m/z: [M+H]⁺: calcd. for [C70H113N8Si4]⁺: 1405.8160; found 1405.8148; correct isotope distribution.

3,3',3'-Tetramethyl-6,6',9,9'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spiro-bi[cyclopenta[b]phenazine] (3e)

The GP was applied to 1 (150 mg, 446 µmol, 1.00 equiv.) and 2e (470 mg, 892 µmol, 2.00 equiv.) in 2.0 mL chloroform and 2.0 mL acetic acid. Flash column chromatography (SiO2; petroleum ether/diethyl ether 250:1 v/v -> 100:1 -> 50:1) and gel permeation chromatography (toluene) yielded green solid 3e (389 mg, 295 µmol, 66 %).

Rf = 0.42 (SiO2; petroleum ether/dichloromethane 2:1, v/v). Mp: 325 °C. 1H NMR (CDCl3, 600 MHz, RT): δ = 7.96 (s, 2H), 7.59 (s, 2H), 2.68 - 2.75 (m, 4H), 1.73 (s, 6H), 1.63 (s, 6H), 1.33 - 1.41 (m, 42H), 1.12 - 1.21 (m, 42H) ppm. 13C NMR (CDCl3, 126 MHz, RT): δ = 160.1, 159.5, 154.8, 154.7, 145.8, 145.7, 142.5, 142.4, 125.0, 122.2, 114.4, 114.1, 111.9, 111.4, 102.3, 102.1, 59.9, 57.3, 44.1, 31.9, 30.4, 19.1, 18.9, 11.8, 11.6 ppm. IR (ATR): ν̃ = 2941, 2862, 1454, 1447, 1364, 1200, 1018, 996, 920, 861, 658, 646, 599, 572 cm⁻¹. HRMS (MALDI⁺) m/z: [M]⁺: calcd. for [C77H113N8Si2S4]⁺: 1316.6897; found 1316.6911; correct isotope distribution. Single crystalline specimen were obtained by slow diffusion of methanol into a chloroform solution of 3e.
Figure S1: Normalized absorption (left) and emission (right) spectra of 3a-e (red) and 4a-e (black) in n-hexane (dilute solution) and thin films on glass (dashed; chloroform, 10 mg mL\(^{-1}\)). 3c-e are non-fluorescent in thin films.
S4. Electrochemistry/cyclovoltammetry

The cyclic voltammetry (CV) experiments were carried out using a platinum working electrode, a platinum wire auxiliary electrode, a silver wire reference electrode, a 0.1 mol L⁻¹ NBu₅PF₆ solution in degassed, dry DCM, and ferrocene/ferrocenium as the reference redox system and internal standard (−5.1 eV) at room temperature and 0.2 V s⁻¹. To determine the first reduction potentials (E₆₀⁻) of 3a-e and the first oxidation potential of ferrocene, the half-wave potentials were used.[2]

**Figure S2:** CV spectrum of 3,3,3′,3′-tetramethyl-6,6′,9,9′-tetrakis((triisopropylsilyl)ethynyl)-2,2′,3,3′-tetrahydro-1,1′-spirobi[cyclopenta[b]phenazine] (3a).

**Figure S3:** CV spectrum of 3,3,3′-Tetramethyl-6,6′,11,11′-tetrakis((triisopropylsilyl)ethynyl)-2,2′,3,3′-tetrahydro-1,1′-spirobi[benzo[b]cyclopenta[i]phenazine] (3b).
Figure S4: CV spectrum of 3,3',3'-tetramethyl-6,6',13,13'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]naphtho[2,3-i]phenazine] (3c).

Figure S5: CV spectrum of 3,3',3'-tetramethyl-6,6',13,13'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]quinoxalino[2,3-i]phenazine] (3d).

Figure S6: CV spectrum of 3,3',3'-tetramethyl-6,6',9,9'-tetrakis((triisopropylsilyl)ethynyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[cyclopenta[b]phenazine] (3e).
S5. Quantum-chemical calculations

Figure S7: Quantum chemical calculations (TURBOMOLE B3LYP/def2-TZVP//Gaussian09 B3LYP/6-311++G**) of the FMOs (LUMOs top, HOMOs bottom) for compounds 4a*-e*. TMS groups were used instead of TIPS.

Figure S8: Quantum chemical calculations (TURBOMOLE B3LYP/def2-TZVP//Gaussian09 B3LYP/6-311++G**) of the FMOs (LUMOs top, HOMOs bottom) for compounds 3a*-e*. TMS groups were used instead of TIPS.
S6. Polarized light microscopy

Figure 9. Microscopic images of spin-coated thin films of 4a-e and 3a-e on glass (chloroform, 10 mg mL⁻¹) under crossed polarizers.
S7. NMR spectra

Figure S10: $^1$H NMR spectrum (600 MHz) of 3a in CDCl$_3$.

Figure S11: $^{13}$C($^1$H) NMR spectrum (151 MHz) of 3a in CDCl$_3$. 
Figure S12: $^1$H NMR spectrum (500 MHz) of 3b in CDCl$_3$.

Figure S13: $^{13}$C($^1$H) NMR spectrum (126 MHz) of 3b in CDCl$_3$. 
Figure S14: $^1$H NMR spectrum (600 MHz) of 3c in CDCl$_3$.

Figure S15: $^{13}$C($^1$H) NMR spectrum (151 MHz) of 3c in CDCl$_3$. 
Figure S16: $^1$H NMR spectrum (500 MHz) of 3d in CDCl$_3$.

Figure S17: $^{13}$C($^1$H) NMR spectrum (126 MHz) of 3d in CDCl$_3$. 

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**Figure S18**: $^1$H NMR spectrum (600 MHz) of 3e in CDCl$_3$.

**Figure S19**: $^{13}$C($^1$H) NMR spectrum (126 MHz) of 3e in CDCl$_3$.
S8. X-ray single-crystal structure analysis

Figure S20: Left: ORTEP structure of 1 (CCDC 1958581); right: bond lengths, measured in black, calculated (TURBOMOLE B3LYP/def2-TZVP) in red.

Empirical formula $\text{C}_{21}\text{H}_{20}\text{O}_4$

Formula weight 336.37

Temperature 200(2) K

Wavelength 0.71073 Å

Crystal system tetragonal

Space group $\text{P}4_1$

$Z$ 8

Unit cell dimensions $a = 10.7698(13)$ Å $\alpha = 90$ deg.

$b = 10.7698(13)$ Å $\beta = 90$ deg.

$c = 29.980(4)$ Å $\gamma = 90$ deg.

Volume 3477.4(10) Å$^3$

Density (calculated) 1.28 g/cm$^3$

Absorption coefficient 0.09 mm$^{-1}$

Crystal shape brick

Crystal size 0.127 x 0.118 x 0.031 mm$^3$

Crystal colour orange

Theta range for data collection 1.9 to 23.5 deg.

Index ranges $-12 \leq h \leq 11, -12 \leq k \leq 12, -33 \leq l \leq 33$
Reflections collected 18481
Independent reflections 5124 (R(int) = 0.0990)
Observed reflections 3435 (I > 2σ(I))
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.96 and 0.74
Refinement method Full-matrix least-squares on F^2
Data/restraints/parameters 5124 / 1 / 459
Goodness-of-fit on F^2 1.04
Final R indices (I>2sigma(I)) R1 = 0.068, wR2 = 0.168
Absolute structure parameter 0.1(10)
Largest diff. peak and hole 0.38 and -0.26 eÅ⁻³

**Figure S21:** ORTEP structure of 3c (CCDC 1958582).

Empirical formula C₉₃H₁₁₆N₄Si₄
Formula weight 1402.25
Temperature 200(2) K
Wavelength 1.54178 Å
Crystal system orthorhombic

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| Property                                      | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Space group                                  | Pccn                                       |
| Z                                            | 4                                          |
| Unit cell dimensions                         | a = 17.2322(13) Å  \( \alpha = 90 \) deg. |
|                                              | b = 33.906(4) Å  \( \beta = 90 \) deg.    |
|                                              | c = 14.9653(12) Å  \( \gamma = 90 \) deg.|
| Volume                                       | 8743.7(14) Å³                              |
| Density (calculated)                         | 1.07 g/cm³                                 |
| Absorption coefficient                       | 0.96 mm⁻¹                                  |
| Crystal shape                                | plank                                      |
| Crystal size                                 | 0.142 x 0.085 x 0.025 mm³                  |
| Crystal colour                               | green                                      |
| Theta range for data collection              | 4.1 to 47.8 deg.                           |
| Index ranges                                 | -16 ≤ h ≤ 13, -32 ≤ k ≤ 32, -14 ≤ l ≤ 14  |
| Reflections collected                        | 30793                                      |
| Independent reflections                      | 4043 (R(int) = 0.1269)                     |
| Observed reflections                         | 2420 (I > 2σ(I))                          |
| Absorption correction                        | Semi-empirical from equivalents            |
| Max. and min. transmission                   | 1.48 and 0.77                              |
| Refinement method                            | Full-matrix least-squares on F²            |
| Data/restraints/parameters                    | 4043 / 973 / 538                           |
| Goodness-of-fit on F²                         | 1.12                                       |
| Final R indices (I>2sigma(I))                | R1 = 0.119, wR2 = 0.273                    |
| Largest diff. peak and hole                  | 0.35 and -0.32 eÅ⁻³                        |
**Figure S22:** Left: ORTEP structure of 3e (CCDC 1958583); right: bond lengths, measured in black, calculated (TURBOMOLE B3LYP/def2-TZVP) in red.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | $C_{77}H_{104}N_8S_2Si_4$                  |
| Formula weight                        | 1318.16                                    |
| Temperature                           | 200(2) K                                   |
| Wavelength                            | 1.54178 Å                                  |
| Crystal system                        | orthorhombic                               |
| Space group                           | $P_{na2_1}$                                |
| $Z$                                   | 4                                          |
| Unit cell dimensions                  |                                            |
| $a = 14.9932(7)$ Å                    | $\alpha = 90$ deg.                        |
| $b = 16.6654(7)$ Å                    | $\beta = 90$ deg.                         |
| $c = 30.2092(19)$ Å                   | $\gamma = 90$ deg.                        |
| Volume                                | $7548.3(7)$ Å                              |
| Density (calculated)                  | 1.16 g/cm$^3$                              |
| Absorption coefficient                | 1.60 mm$^{-1}$                             |
| Crystal shape                         | plank                                      |
| Crystal size                          | $0.175 \times 0.070 \times 0.017$ mm$^3$ |
Crystal colour: green

Theta range for data collection: 3.0 to 48.5 deg.

Index ranges: 
-14 ≤ h ≤ 14, -16 ≤ k ≤ 10, -29 ≤ l ≤ 29

Reflections collected: 29080

Independent reflections: 7041 (R(int) = 0.1502)

Observed reflections: 3818 (I > 2σ(I))

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 1.46 and 0.78

Refinement method: Full-matrix least-squares on F²

Data/restraints/parameters: 7041 / 1801 / 821

Goodness-of-fit on F²: 1.02

Final R indices (I>2sigma(I)): R1 = 0.082, wR2 = 0.176

Absolute structure parameter: 0.41(6)

Largest diff. peak and hole: 0.60 and -0.37 eÅ⁻³

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