

## Electronically Supplementary Information

# Tetraazapentacene Constructs: On Controlling Bulk-Morphology through Molecular Dimensionality

Florian L. Geyer,<sup>a</sup> \* Silke Koser,<sup>a</sup> Maximilian N. Bojanowski,<sup>a</sup> Florian Ullrich,<sup>b, d</sup> Victor Brosius,<sup>a</sup> Sebastian Hahn,<sup>a</sup> Kerstin Brödner,<sup>a</sup> Eric Mankel,<sup>b, d</sup> Tomasz Marszalek,<sup>a, b</sup> Wojciech Pisula,<sup>c, e</sup> Felix Hinkel,<sup>a, b</sup> Uwe H. F. Bunz<sup>a, b\*</sup>

a) Organisch Chemisches Institut, Im Neuenheimer Feld 271, 62912 Heidelberg, Germany

b) Centre for Advanced Materials, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany

c) InnovationLab GmbH, Speyerer Straße 4, 69115 Heidelberg, Germany

d) Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

e) Technische Universität Darmstadt, Materials Science Institute, Surface Science Division, Jovanka-Bontschits-Straße 2, 64287 Darmstadt

f) Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland

# Index

<b>1</b>	<b>General Remarks.....</b>	<b>3</b>
<b>2</b>	<b>Syntheses of TIPSTAP-Constructs .....</b>	<b>5</b>
<b>3</b>	<b>NMR-Spectroscopy.....</b>	<b>16</b>
<b>4</b>	<b>IR-Spectroscopy .....</b>	<b>24</b>
<b>5</b>	<b>UVVis-Spectroscopy.....</b>	<b>27</b>
<b>6</b>	<b>Cyclic Voltammetry .....</b>	<b>30</b>
<b>7</b>	<b>Analytical Gel Permeation Chromatography .....</b>	<b>32</b>
<b>8</b>	<b>Computational Chemistry .....</b>	<b>39</b>
<b>9</b>	<b>XP- and UP-Spectroscopy .....</b>	<b>44</b>
<b>10</b>	<b>Diffractionmetric Characterizations .....</b>	<b>56</b>
<b>11</b>	<b>Summarized Data.....</b>	<b>59</b>
	<b>References .....</b>	<b>59</b>

# 1 General Remarks

All reagents were obtained from commercial suppliers and were used without further purification if not otherwise stated. All cross couplings were carried out within a nitrogen filled glovebox. Absolute solvents were purchased from commercial suppliers (glove box) or dried with an MBraun MB SPS-800 solvent purification system (for Schlenk techniques). Deuterated solvents were purchased from Deutero GmbH, Kastellaun (Germany). Thin films were prepared by drop casting or spin coating on Menzel glass slides (Thermo Scientific). For spin coating, a S.P.S Spin 150 was used.

**Preparative Gel Permeation Chromatography (GPC):** Performed on Bio-Beads S-X1™ polystyrene beads (200 - 400 mesh, Bio-Rad). If not stated otherwise, the chromatography was performed on a 150 cm column (6 cm inner diameter) using toluene as eluent.

**Analytical Gel Permeation Chromatography (GPC):** Mass average molar masses ( $M_w$ ) and polydispersity indices ( $D = M_n/M_w$ ) of macromolecules were assessed by an analytical gel permeation chromatography setup containing a DG-2080-53, a LV-2080-03 and a PU-2080 fitted with a UV-2075 detector and a RI-2031 refractometer (Jasco). Calibration was achieved using three standards containing each four near-monodisperse polystyrene probes. Measurements were carried out at room temperature in stabilizer free tetrahydrofuran with PSS-SDV columns (8.0 mm × 30.0 mm, 5 μm particles, 10<sup>2</sup>-, 10<sup>3</sup>-, 10<sup>5</sup> Å pore size).

**NMR Spectroscopy:** NMR spectra (<sup>1</sup>H, <sup>13</sup>C coupling experiments) were recorded on a Bruker DRX 300 (300 MHz), Bruker Avance III 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) or Bruker Avance III 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million [ppm] relative to traces of [H<sub>1</sub>] solvent in the corresponding deuterated solvent. <sup>1</sup>H NMR spectra assignments are reported as follows (s = singlet, d = doublet, t = triplet, m = multiplet, coupling constant(s) in Hz; integration). Carbon signals were assigned using DEPT-experiments All NMR spectra were integrated and processed by using ACD/Spectrus Processor 2012 release.

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

**High Resolution Mass Spectrometry (HR-MS):** Recorded by the University of Heidelberg Mass Spectrometry Facility using the following instruments: JEOL JMS-700 magnetic sector (EI, CI, FAB, FI, FD, LIFDI); Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, MALDI, DART), Finnigan LCQ quadrupole ion trap (ESI); JEOL AccuTOF GCx time-of-flight (EI, CI); Bruker AutoFlex Speed time-of-flight (LDI, MALDI).

**Infrared (IR) Spectroscopy:** IR spectra were recorded neat on a Jasco FT/IR-4100 spectrometer. Signals are reported in wavenumbers [cm<sup>-1</sup>].

**Photographs:** Photographs were taken under UV-light irradiation (λ = 365 nm) or ambient light using a Canon EOS 7D camera equipped with a Canon EF-S 66 mm objective.

**UV-Vis Spectroscopy:** Absorption spectra were recorded on a Jasco UV-VIS V-660 or 670 Spectrophotometer.

**X-ray and UV photoelectron spectroscopy (XPS and UPS):** The photoelectron spectroscopy experiments were performed at the integrated UHV system “Clustertool” at the InnovationLab in Heidelberg. A Phi VersaProbe II spectrometer was used equipped with a monochromatized Al-K $\alpha$  X-ray source and a gas discharge lamp operated with helium (HeI:  $h\nu = 21.22$  eV) as excitation sources for XPS and UPS, respectively. The energetic resolution determined by the  $2\sigma$ Gaussian broadening used to fit the Fermi edge of a freshly sputter-cleaned silver sample measured at room temperature is 0.35 eV for XPS and 0.13 eV for UPS. All spectra are referenced in binding energy to the Fermi level. The core level lines of in situ cleaned Au, Ag and Cu metal foils were used to calibrate the XPS binding energy scale. While binding energy values are given to the 10 meV digit to track relative changes, the absolute values should be rounded to the next 100 meV digit. Oxygen peaks are attributed to the used substrates (silicon with naturally grown silicon dioxide); also compare Si2p-core level peaks.

**Powder X-ray diffraction (P-XRD)** was carried out using a Siemens D-500 X-ray powder diffractometer equipped with a nickel-filtered Cu-K $\alpha$ 1: 0.1541nm beam, using current  $I = 40$  mA and accelerating voltage  $U = 40$  kV. Data processing and analysis was performed by using the software package Datasqueeze (<http://www.datasqueezesoftware.com>).

**Cyclic Voltammetry:** A Princeton Applied Research VersaSTAT 3 Potentiostat was used. Cyclic voltammetry was performed in DCM solutions of the respective molecule using Bu<sub>4</sub>NPF<sub>6</sub> as an electrolyte, a glassy carbon (PEEK) working electrode, silver wire or Au reference electrode and Pt-coated Ti counter electrode. For the estimation of the FMO-energies, ferrocene was added as an internal standard. For the HOMO of ferrocene, an energy of -4.8 eV was assumed, allowing to estimate the FMO-energies from the determined reduction potentials.[S1]

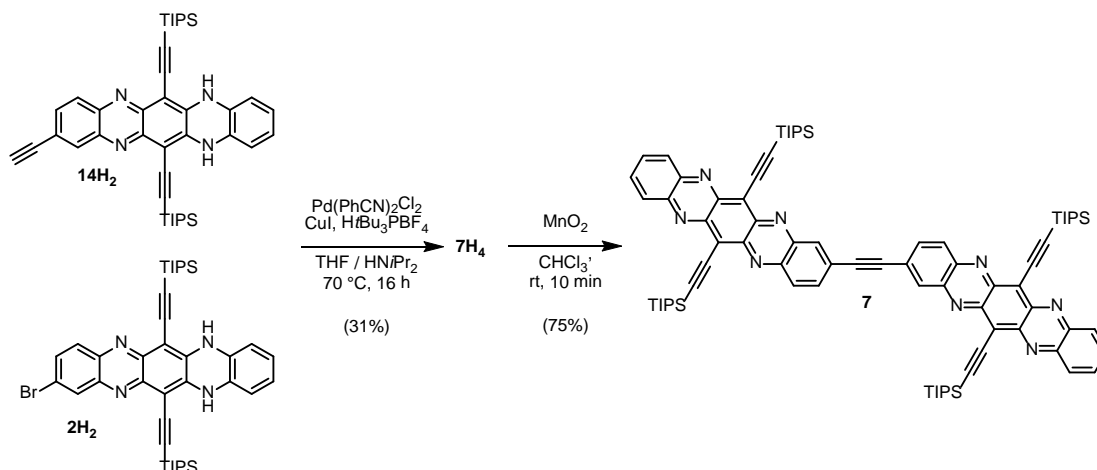
## 2 Syntheses of TIPSTAP-Constructs

### 2.1 Educts and TIPSPen-Cross 12

Synthetic procedures for following compounds have been described elsewhere: **TIPSPen**: Anthony *et al.*,[S2] **TIPSTAP**: Bunz *et al.*[S3] Brominated TIPSTAP **2** and its reduced form **2H<sub>2</sub>**, monoalkynylated species **4**, **5**, **6** as well as the tetraphenylphenyl substituted **1**, their morphological and electronic properties are detailed in a recent study.[S4] We recently described the synthesis, electronic and morphological properties of **TIPSPen-Onsager cross 12**. [S5] An optimized protocol for the tetrahedral alkyne **3** can be found in a recent study.[S6]

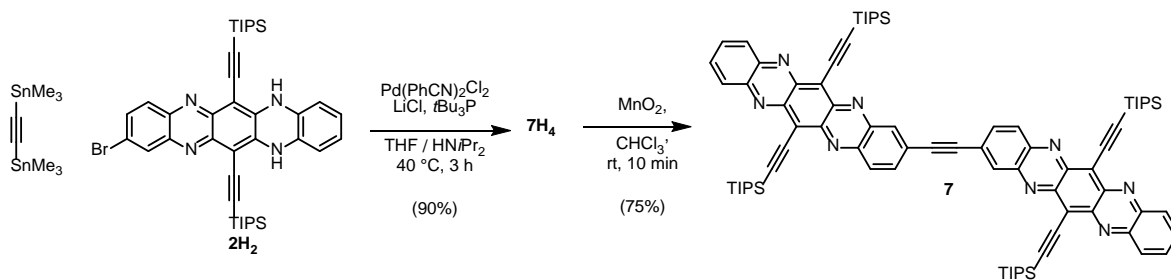
### 2.2 1,2-Bis(6,13-bis(triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethyne (7)

**Method A; by Sonogashira Coupling of 2H<sub>2</sub> with 14H<sub>2</sub>:**



Freshly prepared **14H<sub>2</sub>** (91.6 mg, 137  $\mu$ mol, 1.00 equiv.) and **2H<sub>2</sub>** (119 mg, 164  $\mu$ mol, 1.20 equiv.) were dissolved in dry tetrahydrofuran (8 mL) and degassed. copper(I) iodide (2.61 mg, 13.7  $\mu$ mol 0.20 equiv.), bis(benzonitrile)palladium(II) dichloride (5.25 mg, 13.7  $\mu$ mol, 0.10 equiv.) and tris(*tert*-butylphosphine)tetrafluoroborate (7.94 mg, 27.8  $\mu$ mol, 0.20 equiv.) were added to an oxygen free mixture of tetrahydrofuran / diisopropylamine 1:1 (8 mL) in this sequence. The catalyst solution was stirred for 5 min at room temperature and added to the educt solution. The mixture was stirred at 70 °C for 16 h. The reaction was quenched by addition of DI water (20 mL) and the mixture extracted with dichloromethane (3  $\times$  30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvent evaporated and the residual material subjected to column chromatography (silica, petrol ether / dichloromethane 2:3). *R<sub>f</sub>* (silica, petrol ether / dichloromethane 2:3) = 0.52. Yield: 56.0 mg (42.7  $\mu$ mol), 31%.

## Method B; by Stille coupling of bis(trimethylstannyl)acetylene with 2H<sub>2</sub>:



Within the inert atmosphere of a nitrogen filled glovebox, **2H<sub>2</sub>** (322 mg, 445 μmol, 2.20 equiv.), bis(trimethylstannyl)acetylene (71.1 mg, 202 μmol, 1.00 equiv.) and lithium chloride (51.4 mg, 1.21 mmol, 6.00 equiv.) were dissolved in dry tetrahydrofuran (4 mL) in a glass tube. In a separate tube, bis(benzonitrile)palladium(II) dichloride (4.65 mg, 12.1 μmol, 0.06 equiv.) and tris(*tert*-butyl)phosphine (4.91 mg, 24.3 μmol, 0.12 equiv.) were dissolved in dry tetrahydrofuran (2 mL), stirred for 5 minutes and transferred to the educt tube. The tube was sealed and stirred for 3 h at 40 °C after which analytical GPC indicated the conversion to be complete. The tube was transferred out of the glovebox, the solution filtered over a short silica plug and purified by preparative GPC (toluene). Yield: 200 mg (153 μmol), 75%.

**7H<sub>4</sub>** (200 mg, 153 μmol, 1.00 equiv.) was dissolved in chloroform. manganese dioxide (1.06 g, 12.2 mmol, 80 equiv.) was added, stirred for 10 min at room temperature and the solid residue removed by filtration. The solvent was removed and the residual dark material filtered through a short silica plug (tetrahydrofuran), and purified by preparative GPC (toluene). Yield: 180 mg (137 μmol), 90%.

### Total yields (two steps):

Sonogashira-Route: 28%

Stille-Route: 68%

### Analytical data for 7H<sub>4</sub>:

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **7**.

**IR (neat):**  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3375, 3061, 2940, 2889, 2862, 2141, 1727, 1596, 1574, 1447, 1383, 1366, 1339, 1309, 1290, 1259, 1221, 1099, 1073, 1014, 995, 919, 880, 829, 799, 747.

**UV-Vis:**  $\lambda_{\max}$  = 548 nm.

**HR-MS (MALDI):** [M-2H+H]<sup>+</sup>: m/z calcd. for (C<sub>82</sub>H<sub>101</sub>N<sub>8</sub>Si<sub>4</sub>): 1309.72263, found: 1309.72208.

**Analytical GPC:** M<sub>w</sub> = 1533, D = 1.022, V<sub>Elu</sub> = 27.74 mL.

### Analytical data for 7:

**M.p.:** >400 °C.

**<sup>1</sup>H-NMR (500.13 MHz, d<sub>4</sub>-o-dichlorobenzene, 100 °C):** δ [ppm] = 8.82 (m, 2H), 8.42-8.35 (m, 4H), 8.22-8.18 (m, 2H), 7.90-7.86 (m, 2H), 7.85-7.79 (m, 4H), 7.56-7.53 (m, 2H), 1.70-1.63 (m, 42H), 1.62-1.57 (m, 42H).

As the materials solubility is too low for fully resolved 1D <sup>13</sup>C {<sup>1</sup>H} NMR experiments, a DEPT-135 experiment was used to probe the aromatic CH-groups. The quaternary carbon atoms remain invisible.

**<sup>13</sup>C-DEPT-135-NMR (125.76 MHz, d<sub>4</sub>-o-dichlorobenzene, 100 °C):** δ [ppm] = 133.79 (CH), 133.33 (CH), 131.47 (CH), 130.41 (CH), 130.11 (CH), 129.94 (CH), 126.96 (CH), 18.71 (CH/CH<sub>3</sub>), 18.69 (CH/CH<sub>3</sub>), 11.78 (CH/CH<sub>3</sub>).

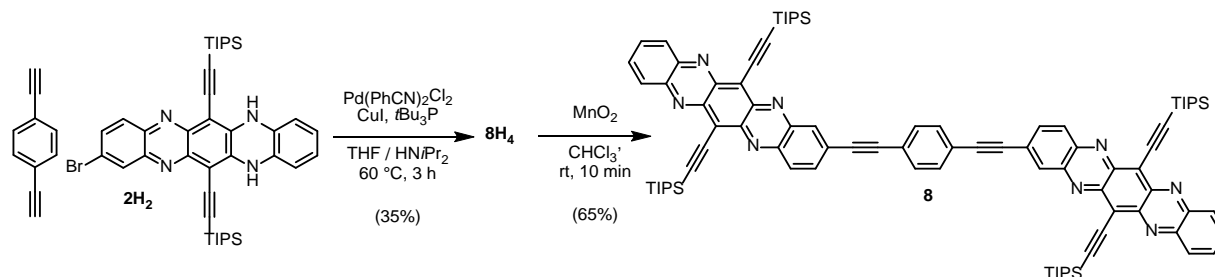
**IR (neat):**  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3067, 2940, 2889, 2862, 1723, 1617, 1523, 1490, 1461, 1435, 1383, 1362, 1324, 1310, 1259, 1233, 1222, 1169, 1135, 1114, 1073, 1020, 994, 920, 881, 831, 816, 748.

**UV-Vis:**  $\lambda_{\text{max}}$  = 700 nm.

**HR-MS (MALDI):** [M]<sup>+</sup>: m/z caclcd. for C<sub>82</sub>H<sub>98</sub>N<sub>8</sub>Si<sub>4</sub>: 1306.6992, found: 1306.70197, correct isotope distribution.

**Analytical GPC:** M<sub>W</sub> = 1503, D = 1.010, V<sub>Elu</sub> = 27.75 mL.

### 2.3 1,4-Bis((6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethynyl)benzene (8)



Under nitrogen atmosphere, tetrakis(triphenylphosphine)palladium(0) (19.60 mg, 16.96  $\mu\text{mol}$ , 0.10 equiv.), copper(I) iodide (33.9 mg, 17.0  $\mu\text{mol}$ , 0.10 equiv.) was added to of a mixture tetrahydrofuran / triethylamine 1:1 (3 mL) and stirred for 5 min at room temperature. 1,4-diethynylbenzene (21.40 mg, 170  $\mu\text{mol}$ , 1.00 equiv) and **2H<sub>2</sub>** (270 mg, 373  $\mu\text{mol}$ , 2.20 equiv.) were dissolved in tetrahydrofuran / triethylamine 1:1 (2 mL) and the catalyst solution transferred into the educt solution. The mixture was stirred at 60 °C and the reaction closely monitored by analytical GPC. After 3 h, when almost all educt was consumed and a polymeric side product started to form the reaction was quenched by a quick filtration over a silica plug followed by preparative GPC (toluene) to yield a dark red solid. Yield: 85.0 mg (224  $\mu\text{mol}$ ), 35% of **8H<sub>4</sub>**. Purification is complicated by the already low solubility of the reduced dimer.

**8H<sub>4</sub>** (37.0 mg, 26.2  $\mu\text{mol}$ , 1.00 equiv.) was dissolved in chloroform (50 mL), manganese dioxide (182 mg, 2.10 mmol, 80 equiv.) was added and the mixture stirred at room temperature for 10 min. The

material has a very low solubility, but forms an oversaturated solution during the oxidation reaction. This oversaturated mixture was poured on a silica plug, which was eluted with further chloroform to yield a dark brown solution. Upon storage, precipitate forms. Removing the solvent yields a dark, black solid. Analytical GPC proves purity of the material. Due to its very low solubility, no further purification was carried out. Yield: 23.8 mg (16.90  $\mu\text{mol}$ ), 65%.

Overall yield from  $2\text{H}_2$ : 23%.

#### **Analytical data for $8\text{H}_4$ :**

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **8**.

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3383, 2924, 2860, 2132, 1712, 1455, 1015, 882, 749.

**UV-Vis:**  $\lambda_{\text{max}}$  = 551 nm.

**HR-MS (MALDI<sup>+</sup>):**  $[\text{M}+\text{H}]^+$ :  $m/z$  calcd. for ( $\text{C}_{90}\text{H}_{107}\text{N}_8\text{Si}_4$ ): 1411.770, found: 1411.763, correct isotope distribution.

**Analytical GPC:**  $M_{\text{W}}$  = 1738 g/mol,  $D$  = 1.013,  $V_{\text{Elu}}$  = 27.47 mL.

#### **Analytical data for **8**:**

**M.p.:** > 400 °C.

**NMR-spectroscopy:** Due to the strong tendency of the material to form aggregates and precipitate, NMR-spectroscopy was carried out in  $d_4$ -dichlorobenzene at 100 °C. Even at this temperature, aggregated material can be seen in the spectra. Two signal patterns (A, B) could be separated, that are present at an 1:1 ratio. IR confirms that this is not due to reduced compound (no NH-band), GPC confirms the material to be pure. It appears that A is monomeric compound, while B is a higher aggregate.

**$^1\text{H}$  NMR (300.13 MHz,  $d_4$ -o-dichlorobenzene, 100 °C):**  $\delta$  [ppm] = 8.68-8.62 (A, m, 2H), 8.53-8.43 (B, m, 1H), 8.42-8.33 (A, m, 6H), 8.25-8.17 (B, m, 2H), 8.02-7.91 (B, m, 2H), 8.02-7.91 (B, m, 4H), 7.86-7.77 (A, m, 10H), 7.76-7.68 (B, m, 3H), 7.39-7.23 (B, m, 8H), 1.75-1.65 (B, m, 82H), 1.45-1.35 (A, m, 84H).

As the materials solubility is too low for fully resolved 1D  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR experiments, a DEPT-135 experiment was used to sensitize the aromatic CH-groups. The quaternary carbon atoms remain invisible. To calibrate the DEPT, 1D  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR experiments was carried out to visualize the TIPS-carbon atoms and calibrate them to the deuterated solvent. During this experiment, an unassignable signal at 11.45 ppm formed – it remains unclear if this is due to decomposition at the harsh conditions or formation of another aggregated species.

**$^{13}\text{C}$ -DEPT-135-NMR (125.76 MHz,  $d_4$ -dichlorobenzene, 100 °C):**  $\delta$  [ppm] = 18.63 (CH/CH<sub>3</sub>), 18.49 (CH/CH<sub>3</sub>), 18.47 (CH/CH<sub>3</sub>), 11.75 (CH/CH<sub>3</sub>), 11.08 (CH/CH<sub>3</sub>).

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3066, 2941, 2892, 2864, 2359, 2204, 1615, 1460, 1110, 1024, 882, 750.

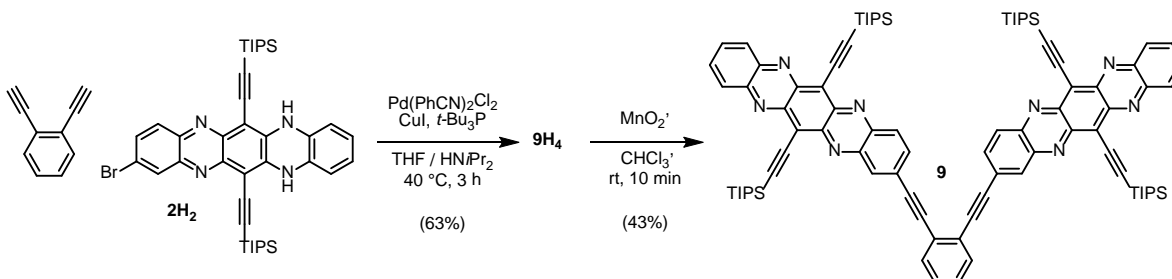


**UV-Vis:**  $\lambda_{\max}$  = 695 nm.

**HR-MS (MALDI):**  $[M+2H]^+$ :  $m/z$  calcd. for  $(C_{90}H_{102}N_8Si_4)$ : 1409.74946, found: 1409.75567, correct isotope distribution.

**Analytical GPC:**  $M_W$  = 1706 g/mol,  $D$  = 1.0131,  $V_{Elu}$  = 27.52 mL.

## 2.4 1,2-Bis((6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethynyl)benzene (9)



Within the inert atmosphere of a nitrogen filled glove box, bis(benzonitrile)dichloropalladium(II) (16.3 mg, 42.4  $\mu$ mol, 0.15 equiv.), copper(I) iodide (8.07 mg, 42.4  $\mu$ mol, 0.15 equiv.) and tris(*tert*-butyl)phosphine (17.2 mg, 85  $\mu$ mol, 0.30 equiv.) was added to of a mixture tetrahydrofuran / diisopropylamine 2:1 (3 mL) and stirred for 5 min at room temperature. 1,2-diethynylbenzene (35.6 mg, 283  $\mu$ mol, 1.00 equiv.) and 2H<sub>2</sub> (450 mg, 622  $\mu$ mol, 2.20 equiv.) were dissolved in tetrahydrofuran / diisopropylamine 2:1 (2 mL) and the catalyst solution transferred into the educt solution. It was stirred at 40 °C and the reaction closely monitored by analytical GPC. After 3 h, when almost all educt was consumed and a polymeric side product started to form the reaction was quenched by a quick filtration over a silica plug followed by preparative GPC on toluene to yield a dark red solid. Yield: 251 mg (178  $\mu$ mol), 63% of 9H<sub>4</sub>.

9H<sub>4</sub> (251 mg, 178  $\mu$ mol) was dissolved in chloroform (50 mL) at room temperature, manganese dioxide (1.23 g, 14.20 mmol, 80 equiv.) were added and the mixture stirred for 10 min and filtered over a silica plug (CHCl<sub>3</sub>). Preparative GPC (toluene) yielded a black, amorphous substance. Yield: 224 mg (91.0  $\mu$ mol), 43%.

Overall yield: 27%

### **Analytical data for 9H<sub>4</sub>:**

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to 9.

**IR (neat):**  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3375, 3058, 2940, 2890, 2863, 2204, 2142, 1576, 1454, 1016, 747.

**UV-Vis:**  $\lambda_{\max}$  = 544 nm.

**HR-MS (MALDI<sup>+</sup>):**  $[M+H]^+$ :  $m/z$  calcd. for  $(C_{90}H_{107}N_8Si_4)$ : 1411.770, found: 1411.759, correct isotope distribution.

**Analytical GPC:**  $M_w = 1390$ ,  $D = 1.011$ ,  $V_{Elu} = 27.92$  mL.

**Analytical data for 9:**

**M.p.:** > 400°C.

**$^1\text{H-NMR}$  (500.13 MHz, *o*-Dichlorbenzol- $d_4$ , 22 °C):**  $\delta$  [ppm] = 8.82-8.78 (m, 2H), 8.50-8.45 (m, 2H), 8.42-8.35 (m, 4H), 8.22-8.18 (m, 2H), 7.90-7.86 (m, 2H), 8.85-7.79 (m, 4H), 7.56-7.53 (m, 2H), 1.70-1.63 (m, 42H), 1.62-1.57 (m, 42H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR (125.76 MHz, *o*-Dichlorbenzol- $d_4$ , 22 °C):**  $\delta$  [ppm] = 142.21 ( $C_q$ ), 145.15 ( $C_q$ ), 144.75 ( $C_q$ ), 144.70 ( $C_q$ ), 143.08 ( $C_q$ ), 142.86 ( $C_q$ ), 142.82 ( $C_q$ ), 142.58 ( $C_q$ ), 133.99 (CH), 133.19 (CH), 132.48 (CH), 131.95 ( $C_q$ ), 131.82 (CH), 130.74 (CH), 130.27 (CH), 129.42 ( $C_q$ ), 129.34 ( $C_q$ ), 128.88 (CH), 127.41 ( $C_q$ ), 126.56 ( $C_q$ ), 125.27 ( $C_q$ ), 123.32 ( $C_q$ ), 112.35 ( $C_q$ ), 112.06 ( $C_q$ ), 103.70 ( $C_q$ ), 103.61 ( $C_q$ ), 94.10 ( $C_q$ ), 93.69 ( $C_q$ ), 18.92 (CH/CH<sub>3</sub>), 18.89 (CH/CH<sub>3</sub>), 11.70 (CH/CH<sub>3</sub>), 11.71 (CH/CH<sub>3</sub>).

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3063, 2940, 2889, 2862, 2205, 1613, 1459, 1019, 748.

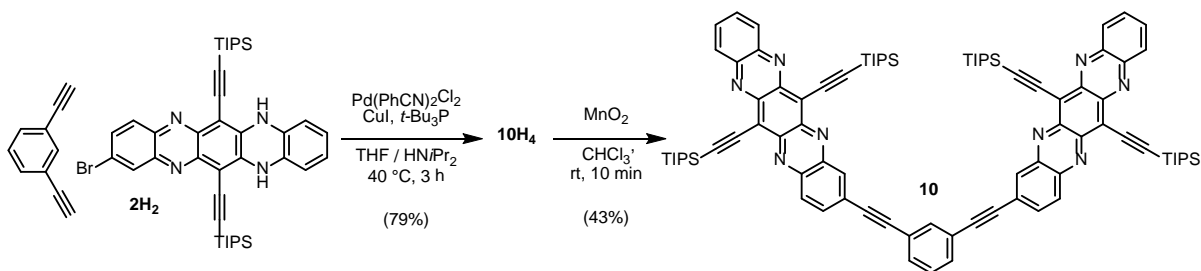
**UV-Vis:**  $\lambda_{\text{max}} = 696$  nm.

**HR-MS (MALDI):** [M]<sup>+</sup>:  $m/z$  calcd. for ( $C_{90}H_{102}N_8Si_4$ ): 1407.734, found: 1407.722, correct isotope distribution.

**Analytical GPC:** MW = 1312, D = 1.012,  $V_{Elu} = 28.00$  mL.

**Cyclic Voltammetry:**  $V_{\text{red1}} = -0.86$  V,  $V_{\text{red2}} = -1.49$  V.

**2.5 1,3-Bis((6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethynyl)benzene (10)**



Within the inert atmosphere of a nitrogen filled glove box, bis(benzonitrile)dichloropalladium(II) (16.3 mg, 42.4  $\mu\text{mol}$ , 0.15 equiv.), copper(I) iodide (8.07 mg, 42.4  $\mu\text{mol}$ , 0.15 equiv.) and tris(*tert*-butyl)phosphine (17.2 mg, 85.0  $\mu\text{mol}$ , 0.30 equiv.) was added to of a mixture tetrahydrofuran / diisopropylamine 2:1 (3 mL) and stirred at room temperature for 5 min. 1,3-diethynylbenzene (35.6 mg, 283  $\mu\text{mol}$ ) and **2H<sub>2</sub>** (450 mg, 622  $\mu\text{mol}$ ) were dissolved in tetrahydrofuran / diisopropylamine 2:1 (2 mL) and the catalyst solution transferred into the educt solution. It was stirred at 40 °C and the reaction closely monitored by analytical GPC. After 3 h, when almost all educt was consumed and a polymeric side product started to form the reaction was quenched by a quick filtration over a

silica plug followed by preparative GPC (toluene) to yield a dark red solid. Yield: 317 mg (224  $\mu\text{mol}$ ), 79% of **10H<sub>4</sub>**.

**10H<sub>4</sub>** (296 mg, 210  $\mu\text{mol}$ ) was dissolved in chloroform (50 mL) at room temperature, manganese dioxide (1.46 g, 16.8 mmol, 80.0 equiv.) were added and the mixture stirred for 10 min and filtered over a silica plug (chloroform). Preparative GPC (toluene) yielded a black, amorphous substance. Yield: 128 mg (91.0  $\mu\text{mol}$ ), 43%.

Overall yield: 34%.

#### **Analytical data for 10H<sub>4</sub>:**

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **10**.

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3379, 2941, 2891, 2864, 2363, 2143, 1576, 1452, 749.

**UV-Vis:**  $\lambda_{\text{max}}$  = 548 nm.

**HR-MS (MALDI<sup>+</sup>):** [M+H]<sup>+</sup>: m/z calcd. for (C<sub>90</sub>H<sub>107</sub>N<sub>8</sub>Si<sub>4</sub>): 1411.770, found: 1411.761, correct isotope distribution.

**Analytical GPC:** M<sub>W</sub> = 1737, D = 1.013, V<sub>Elu</sub> = 27.51 mL.

#### **Analytical data for 10:**

**M.p.:** >400 °C.

**NMR-spectroscopy:** Due to the tendency of the material to form aggregates, NMR-spectroscopy was carried out in d<sub>4</sub>-dichlorobenzene at 100 °C. At this temperature, only minor signals of aggregated material can be seen in the spectra that have been neglected for interpretation.

**<sup>1</sup>H NMR (300.13 MHz, d<sub>4</sub>-o-dichlorobenzene, 100 °C):**  $\delta$  [ppm] = 8.71-8.64 (m, 2H), 8.44-8.32 (m, 6H), 8.13-7.96 (m, 4H), 7.85-7.76 (m, 6H), 1.75-1.60 (m, 84H).

**<sup>13</sup>C {<sup>1</sup>H} NMR (75.47 MHz, d<sub>4</sub>-o-dichlorobenzene, 100 °C):**  $\delta$  [ppm] = 145.14 (C<sub>q</sub>), 145.07 (C<sub>q</sub>), 144.59 (C<sub>q</sub>), 144.51 (C<sub>q</sub>), 142.92 (C<sub>q</sub>), 142.81 (C<sub>q</sub>), 142.71 (C<sub>q</sub>), 142.47 (C<sub>q</sub>), 134.79 (CH), 133.66 (CH), 132.93 (CH), 132.02 (CH), 131.82 (C<sub>q</sub>), 131.38 (CH), 130.32 (C<sub>q</sub>), 130.38 (C<sub>q</sub>), 130.22 (CH), 130.07 (CH), 129.91 (CH), 128.31 (C<sub>q</sub>), 126.90 (CH), 123.20 (C<sub>q</sub>), 123.07 (C<sub>q</sub>), 103.66 (C<sub>q</sub>), 103.55 (C<sub>q</sub>), 94.17 (C<sub>q</sub>), 90.03 (C<sub>q</sub>), 18.65 (CH/CH<sub>3</sub>), 11.75 (CH/CH<sub>3</sub>).

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3066, 2940, 2889, 2862, 2203, 1614, 1460, 749.

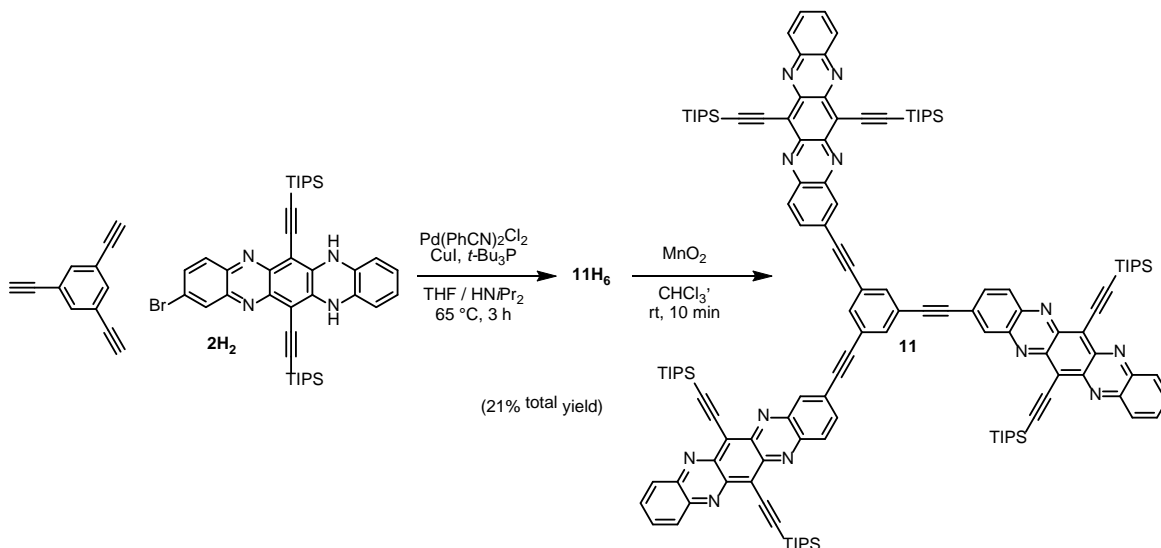
**HR-MS (MALDI<sup>-</sup>):** [M]<sup>-</sup>: m/z calcd. for (C<sub>90</sub>H<sub>102</sub>N<sub>8</sub>Si<sub>4</sub>): 1407.734, found: 1407.738, correct isotope distribution.

**UV-Vis:**  $\lambda_{\text{max}}$  = 694 nm.

**Analytical GPC:** M<sub>W</sub> = 1902, D = 1.014, V<sub>Elu</sub> = 27.35 mL.

**Cyclic Voltammetry:** V<sub>red1</sub> = -0.84 V, V<sub>red2</sub> = -1.30 V.

## 2.6 1,3,5-Tris((6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethynyl)benzene (**11**)



Within the inert atmosphere of a nitrogen filled glovebox, bis(benzonitrile)palladium(II) dichloride (26.7 mg, 69.5  $\mu\text{mol}$ , 0.21 equiv.), copper(I) iodide (6.93 mg, 36.4  $\mu\text{mol}$ , 0.11 equiv.) were added to a mixture tetrahydrofuran / diisopropylamine 2:1 (12 mL) and stirred for 5 min at room temperature. Tris(*tert*-butyl)phosphine (28.1 mg, 139  $\mu\text{mol}$ , 0.42 equiv.) was added and the catalyst solution stirred for another 10 min before it was transferred to tube containing **2H<sub>2</sub>** (800 mg, 1.10 mmol, 3.33 equiv.) and 1,3,5-triethynylbenzene (49.7 mg, 331  $\mu\text{mol}$ , 1.00 equiv.). The stirred reaction mixture was heated to 65 °C and the progressing coupling cascade closely observed by analytical GPC. After 3 h, the reaction was quenched by filtration over a plug of basic aluminum oxide (eluted with tetrahydrofuran). The red, fluorescent solution was evaporated and the residual, red material redissolved in chloroform and purified by a short preparative GPC to remove most side products and excess **2H<sub>2</sub>**. **11H<sub>6</sub>** is best directly oxidized to **11** from this solution. The product fractions of **11H<sub>2</sub>** in chloroform were transferred to a round bottom flask, stirred and an excess of manganese dioxide was suspended in the solution which quickly changed its color from intense red to a dark green. The solid residue was removed by filtration over a plug of basic aluminum oxide, the solvent evaporated and the crude product purified by passing through a preparative GPC column (toluene). Yield: 143 mg (69.0  $\mu\text{mol}$ ), 21%.

### Analytical data for **11H<sub>6</sub>**:

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **11**.

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3378, 3058, 2940, 2922, 2862, 2209, 2140, 1574, 1447, 1015, 748.

**UV-Vis:**  $\lambda_{\text{max}}$  = 549 nm.

**HR-MS (MALDI+):** [M+H]<sup>+</sup>: calcd. for C<sub>132</sub>H<sub>157</sub>N<sub>12</sub>Si<sub>6</sub>: 2078.12698, found: 2078.12439, correct isotope distribution.

**Analytical GPC:**  $M_w = 2545$  g/mol,  $D = 1.008$ ,  $V_{Elu} = 26.75$  mL.

**Analytical data for 11:**

**M.p:**  $>400$  °C

**$^1\text{H}$  NMR (600.24 MHz,  $d_8$ -THF, 22 °C):**  $\delta$  [ppm] = 8.50-8.39 (m, 3H), 8.29-8.25 (m, 3H), 8.24-8.19 (m, 6H), 8.10-8.07 (m, 3H), 8.05-8.01 (m, 3H), 7.95-7.89 (m, 6H), 1.44-1.142 (m, 63H), 1.42-1.40 (m, 63H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR (150.93 MHz,  $d_8$ -THF, 22 °C):**  $\delta$  [ppm] = 146.63 ( $C_q$ ), 146.58 ( $C_q$ ), 146.01 ( $C_q$ ), 145.94 ( $C_q$ ), 144.33 ( $C_q$ ), 144.25 ( $C_q$ ), 144.18 ( $C_q$ ), 143.92 ( $C_q$ ), 136.50 (CH), 135.14 (CH), 134.37 (CH), 133.62 (CH), 131.98 ( $C_q$ ), 131.39 ( $C_q$ ), 127.67 ( $C_q$ ), 124.98 ( $C_q$ ), 124.77 ( $C_q$ ), 112.77 ( $C_q$ ), 112.46 ( $C_q$ ), 104.65 ( $C_q$ ), 104.53 ( $C_q$ ), 93.97 ( $C_q$ ), 91.56 ( $C_q$ ), 19.63 (CH/ $\text{CH}_3$ ), 19.58 (CH/ $\text{CH}_3$ ), 12.84 (CH/ $\text{CH}_3$ ), 12.83 (CH/ $\text{CH}_3$ ).

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] 3066, 2940, 2925, 2893, 2864, 2341, 1461, 1109, 1023, 881, 752, 674.

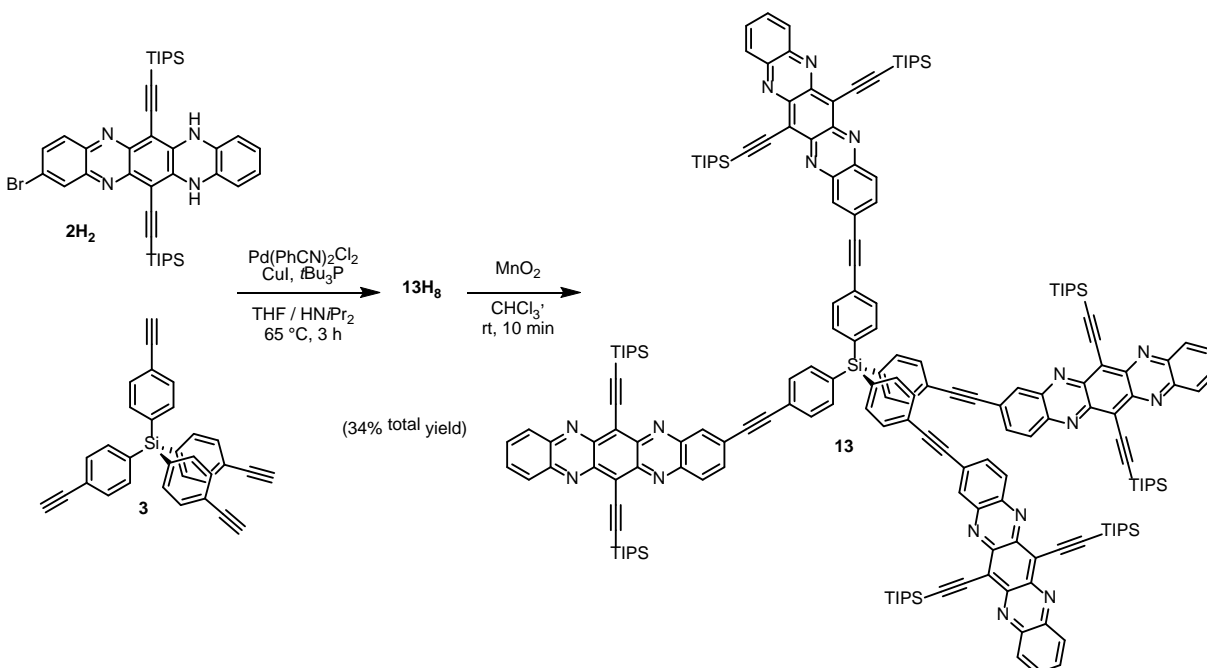
**UV-Vis:**  $\lambda_{\text{max}} = 694$  nm.

**HR-MS (MALDI):**  $[\text{M}+2\text{H}]^+$ : calcd. for  $\text{C}_{132}\text{H}_{152}\text{N}_{12}\text{Si}_6$ : 2073.08785, found: 2073.08667, correct isotope distribution.

**Analytical GPC:**  $M_w = 2462$  g/mol,  $D = 1.011$ ,  $V_{Elu} = 26.82$  mL.

**Cyclic Voltammetry:**  $V_{\text{red1}} = -0.80$  V,  $V_{\text{red2}} = -1.22$  V.

**2.7 Tetrakis(4-((6,13-bis((triisopropylsilyl)ethynyl)-5,7,12,14-tetraazapentacen-2-yl)ethynyl)phenyl)silane (13)**



Within the inert atmosphere of a nitrogen glovebox, bis(benzonitrile)dichloropalladium(II) (7.04 mg, 18.4  $\mu\text{mol}$ , 0.30 equiv.), CuI (1.75 mg, 9.18  $\mu\text{mol}$ , 0.15 equiv.) were added to a mixture tetrahydrofuran / diisopropylamine 2:1 (3 mL) and stirred at room temperature for 5 min. Tris(*tert*-butyl)phosphine (10.7 mg, 36.7  $\mu\text{mol}$ , 0.60 equiv.) was added and the catalyst solution stirred for another 10 min before it was transferred to a flask containing **2H<sub>2</sub>** (200 mg, 275  $\mu\text{mol}$ , 4.50 equiv.) and tetrakis(4-ethynylphenyl)silane (26.5 mg, 61.2  $\mu\text{mol}$ , 1.00 equiv). The stirred reaction mixture was heated to 65 °C and the progressing coupling cascade closely observed by analytical GPC. After 3 h, the reaction was quenched by filtration over a plug of basic aluminum oxide (eluent: tetrahydrofuran). The red, fluorescent solution was evaporated and the residual, red material redissolved in chloroform and purified by a short preparative GPC to remove most side products and excess **2H<sub>2</sub>**. **13H<sub>8</sub>** is best directly oxidized to **13** from this solution. The product fractions of **13H<sub>8</sub>** in chloroform were transferred to a round bottom flask, stirred and an excess of manganese dioxide was suspended in the solution which quickly changed its color from intense red to a dark green. The solid residue was removed by filtration over a plug of basic aluminum oxide, the solvent evaporated and the crude product purified by passing through a preparative GPC column (ca 1.5 m length, toluene). Yield: 59.7 mg (19.9  $\mu\text{mol}$ ), 34%.

#### **Analytical data for 13H<sub>8</sub>:**

**NMR-spectroscopy:** Due to the complex tautomerism, meaningful NMR spectroscopy is best carried out after oxidation to **13**.

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3368, 3061, 2939, 2888, 2862, 2144, 2140, 2135, 2128, 1448, 1260, 1095, 1016, 744.

**UV-Vis:**  $\lambda_{\text{max}}$  = 548 nm.

**HR-MS (MALDI<sup>+</sup>):** [M+H]<sup>+</sup>: calcd. for C<sub>192</sub>H<sub>221</sub>N<sub>16</sub>Si<sub>9</sub>: 3002.57085, found: 3002.57628, correct isotope distribution.

**Analytical GPC:** M<sub>W</sub> = 3934, D = 1.020, V<sub>Elu</sub> = 25.95 mL.

#### **Analytical data for 13:**

**M.p.:** >400 °C

**<sup>1</sup>H NMR (600.24 MHz, d<sub>8</sub>-THF, 25 °C):**  $\delta$  [ppm] = 8.41-8.39 (m, 4H), 8.25-8.19 (m, 12H), 8.02-7.98 (m, 4H), 7.94-7.90 (m, 8H), 7.84-7.76 (m, 16H), 1.41-1.39 (m, 192H).

**<sup>13</sup>C {<sup>1</sup>H} NMR (150.93 MHz, d<sub>8</sub>-THF, 25 °C):**  $\delta$  [ppm] = 146.61 (C<sub>q</sub>), 146.54 (C<sub>q</sub>), 146.01 (C<sub>q</sub>), 145.98 (C<sub>q</sub>), 144.31 (C<sub>q</sub>), 144.22 (C<sub>q</sub>), 144.12 (C<sub>q</sub>), 143.87 (C<sub>q</sub>), 137.61 (CH), 135.88 (C<sub>q</sub>), 135.34 (CH), 134.09 (CH), 133.59 (CH), 132.52 (CH), 131.79 (CH), 131.39 (CH), 128.17 (C<sub>q</sub>), 125.44 (C<sub>q</sub>), 124.21 (C<sub>q</sub>), 112.66 (C<sub>q</sub>), 112.35 (C<sub>q</sub>), 104.64 (C<sub>q</sub>), 104.52 (C<sub>q</sub>), 96.05 (C<sub>q</sub>), 91.40 (C<sub>q</sub>), 19.58 (CH/CH<sub>3</sub>), 19.56 (CH/CH<sub>3</sub>), 12.81 (CH/CH<sub>3</sub>).

**IR (neat):**  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3068, 2940, 2862, 2206, 1614, 1460, 1110, 1019, 881, 752, 675, 587.

**UV-Vis:**  $\lambda_{\max} = 697 \text{ nm}$ .

**HR-MS (MALDI):** [M]<sup>+</sup>: calcd. for C<sub>192</sub>H<sub>212</sub>N<sub>16</sub>Si<sub>9</sub>: 2993.50098, found:2993.50159, correct isotope distribution.

**Analytical GPC:** M<sub>w</sub> = 3583, D = 1.017, V<sub>Elu</sub> = 26.12 mL.

**Cyclic Voltammetry:** V<sub>red1</sub> = -0.79 V, V<sub>red2</sub> = -1.36 V.

### 3 NMR-Spectroscopy

Acquisition Time (sec)	3.2768	Date Stamp	06 Aug 2016 14:54:13	Frequency (MHz)	500.1300	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	49152	Points Count	65536	Receiver Gain	645.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	2493.6978	Sweep Width (Hz)	14999.77	SW(cyclical) (Hz)	15000.00
						Temperature (degree C)	22.000

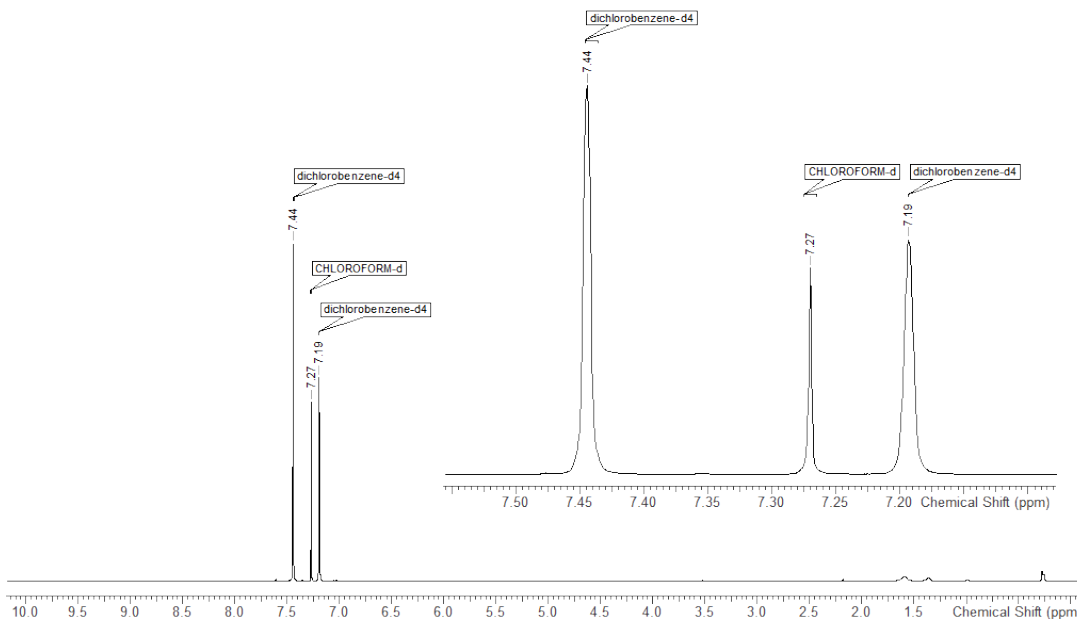


Figure S3.1: <sup>1</sup>H-NMR of a mixture of CDCl<sub>3</sub> and *o*-Dichlorobenzol-d<sub>4</sub> for the calibration of the dichlorobenzene-spectra.

Acquisition Time (sec)	1.7302	Date Stamp	06 Aug 2016 15:23:43	Frequency (MHz)	125.7578	Nucleus	<sup>13</sup> C
Number of Transients	512	Original Points Count	65536	Points Count	65536	Receiver Gain	1620.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	13799.4717	Sweep Width (Hz)	37878.21	SW(cyclical) (Hz)	37878.79
Temperature (degree C)	22.002						

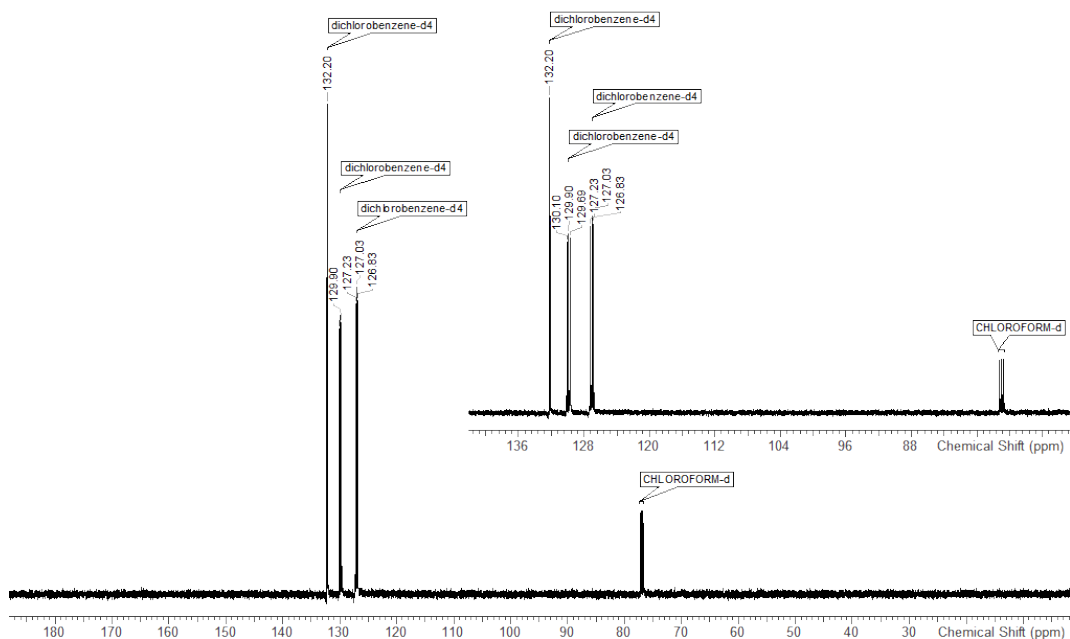


Figure S3.2: <sup>13</sup>C-NMR of a mixture of CDCl<sub>3</sub> and *o*-Dichlorobenzol-d<sub>4</sub> for the calibration of the dichlorobenzene-spectra.



Acquisition Time (sec)	3.2768	Date Stamp	29 Oct 2015 07:43:17	Frequency (MHz)	500.1300	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	49152	Points Count	65536	Receiver Gain	512.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	2469.3413	Sweep Width (Hz)	14999.77	SW (cyclical) (Hz)	15000.00
						Temperature (degree C)	100.117

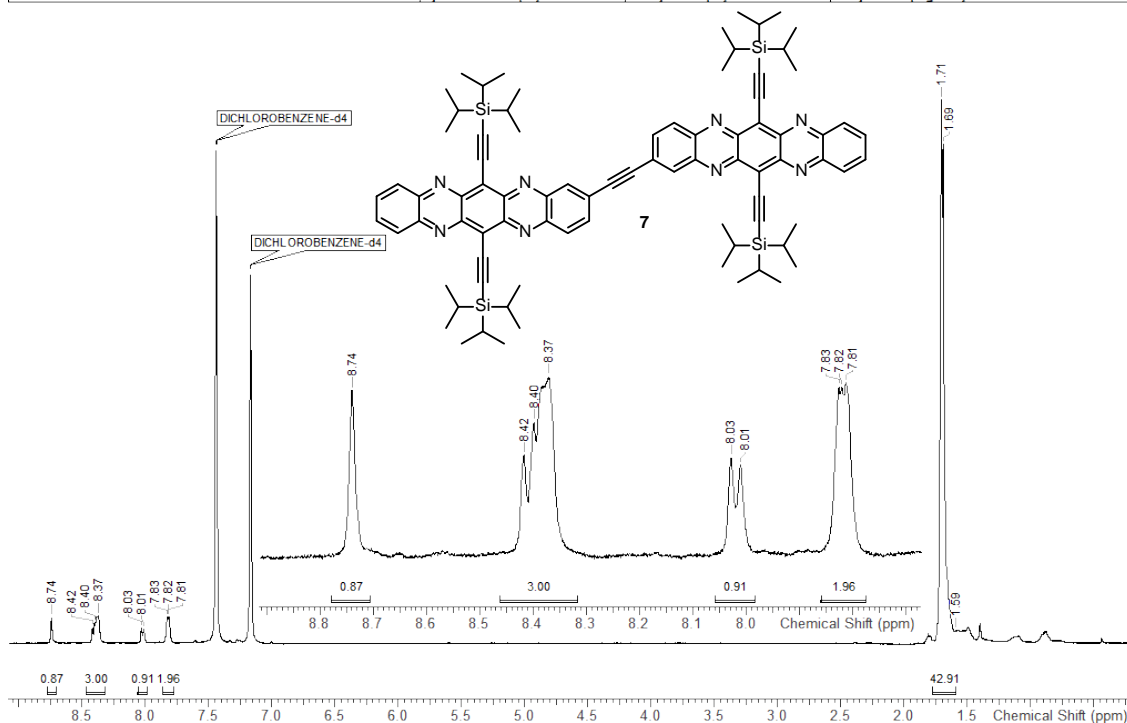


Figure S3.3: <sup>1</sup>H-NMR of 1D-construct 7.

Acquisition Time (sec)	1.7302	Date Stamp	28 Oct 2015 14:49:34	Frequency (MHz)	125.7578	Nucleus	<sup>13</sup> C
Number of Transients	10240	Original Points Count	65536	Points Count	65536	Receiver Gain	1620.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	13762.7119	Sweep Width (Hz)	37878.21	SW (cyclical) (Hz)	37878.79
Temperature (degree C)	100.559						

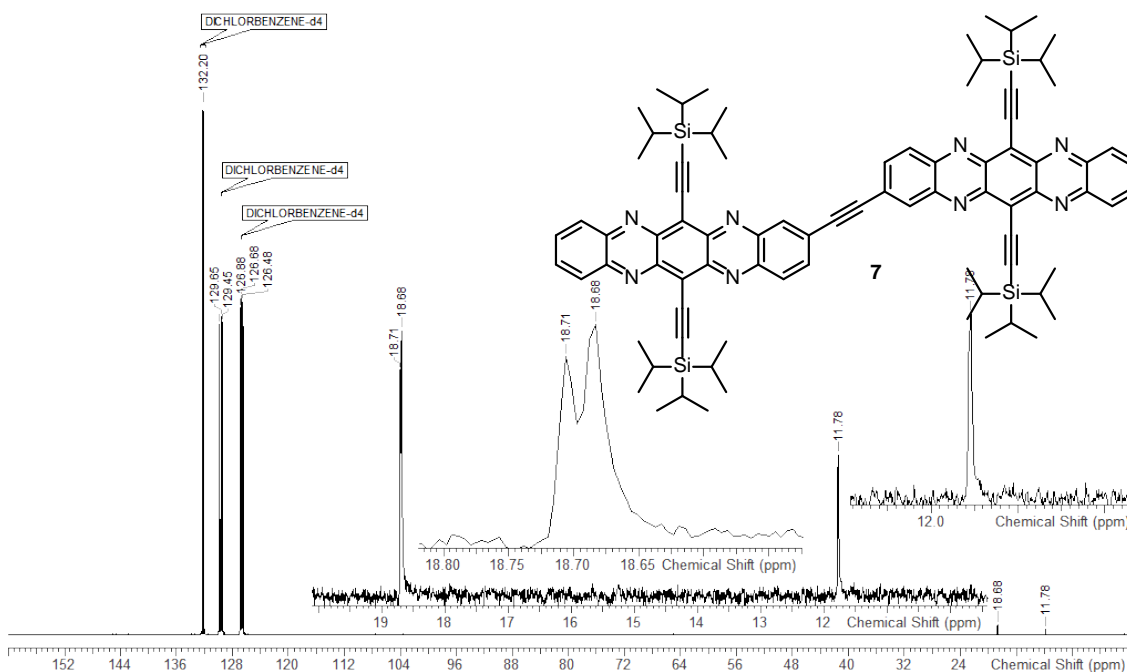


Figure S3.4: <sup>13</sup>C-NMR of 1D-construct 7. Only TIPS-carbons are visible.

Acquisition Time (sec)	1.7302	Date Stamp	29 Oct 2015 00:12:01	Frequency (MHz)	125.7578	Nucleus	<sup>13</sup> C
Number of Transients	4800	Original Points Count	65536	Points Count	65536	Receiver Gain	2050.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	13763.3037	SW(cyclical) (Hz)	37878.79	Sweep Width (Hz)	37878.21
Temperature (degree C)	100.164						

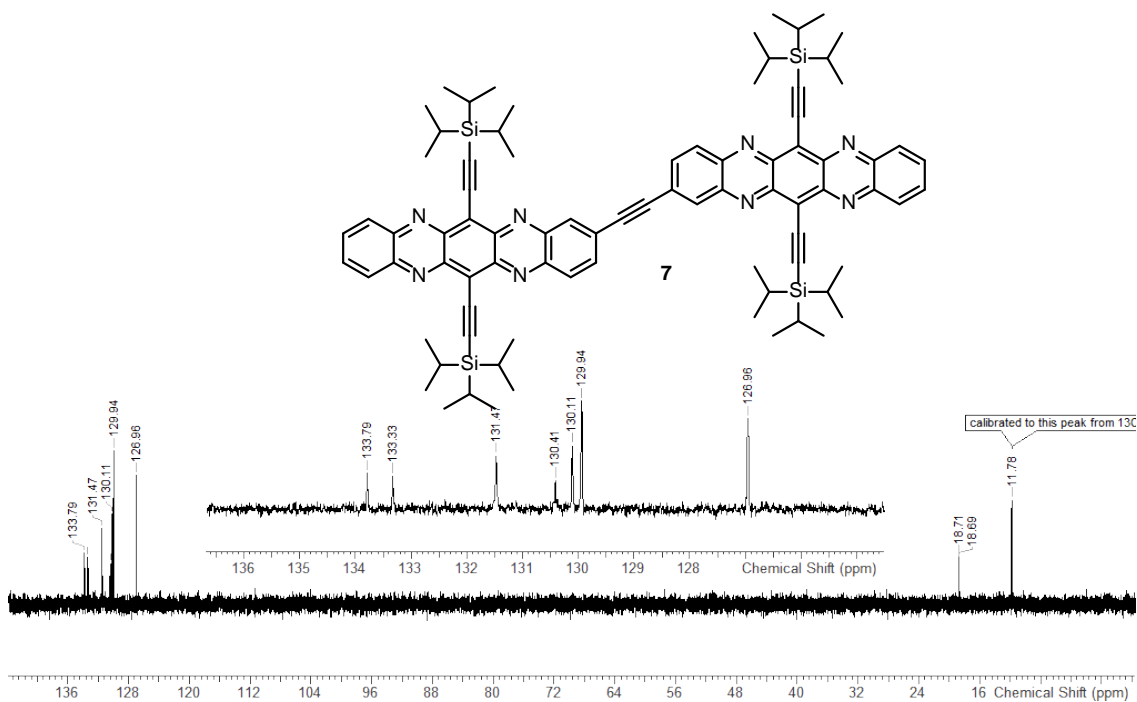


Figure S3.5: DEPT-135-experiment of **7** in *o*-dichlorobenzene-*d*<sub>4</sub> sensitizes CH-carbons.

Acquisition Time (sec)	3.6438	Date Stamp	09 Aug 2016 15:31:25	Frequency (MHz)	300.1300	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	32768	Points Count	32768	Receiver Gain	574.70
Solvent	<i>o</i> -CD <sub>2</sub> Cl <sub>2</sub>	Spectrum Offset (Hz)	1498.1598	SW(cyclical) (Hz)	8992.81	Sweep Width (Hz)	8992.53
Temperature (degree C)	100.160						

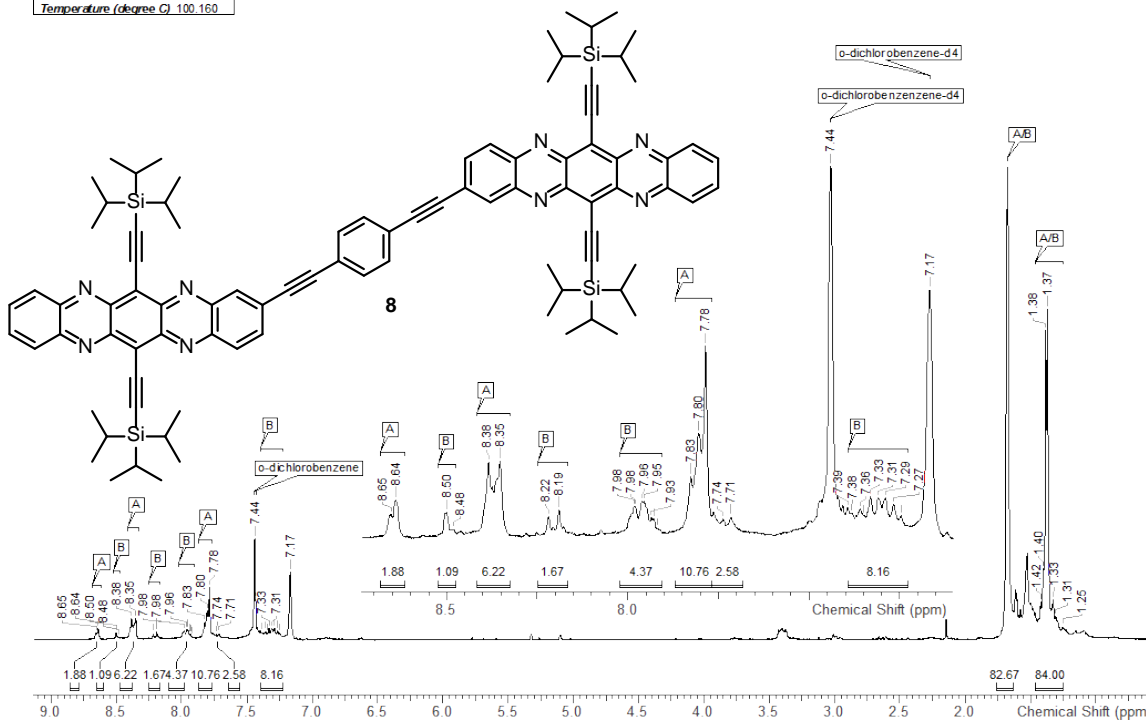


Figure S3.6: <sup>1</sup>H-NMR of 1D-construct **8**.

Acquisition Time (sec)	1.7400	Date Stamp	09 Aug 2016 15:40:01	Frequency (MHz)	75.4678	Nucleus	<sup>13</sup> C
Number of Transients	19200	Original Points Count	32768	Points Count	65536	Receiver Gain	6502.00
Solvent	c6d4c12	Spectrum Offset (Hz)	8260.8711	Sweep Width (Hz)	18832.11	Temperature (degree C)	100.160

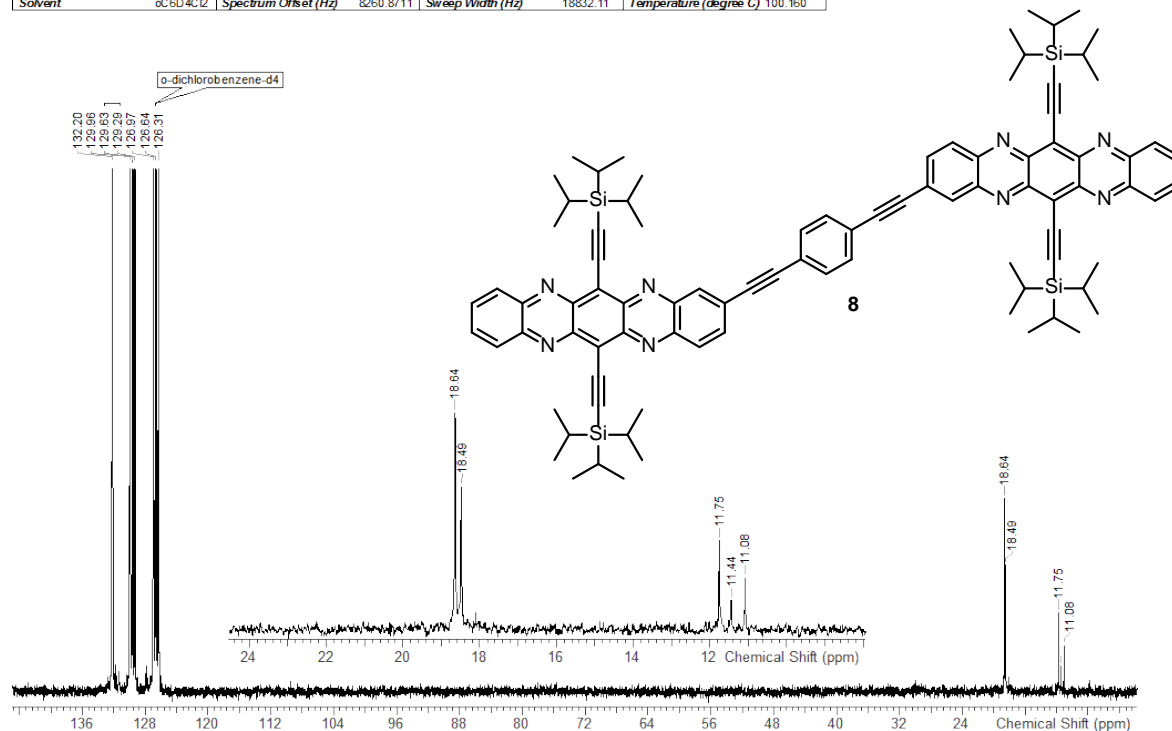


Figure S3.7: <sup>13</sup>C-NMR of construct 8. Only TIPS-carbons are visible.

Acquisition Time (sec)	3.2768	Date Stamp	07 Aug 2016 23:42:15	Frequency (MHz)	500.1300	Nucleus	<sup>1</sup> H
Number of Transients	512	Original Points Count	49152	Points Count	65536	Receiver Gain	181.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	2802.9758	Sweep Width (Hz)	14999.77	Temperature (degree C)	22.004

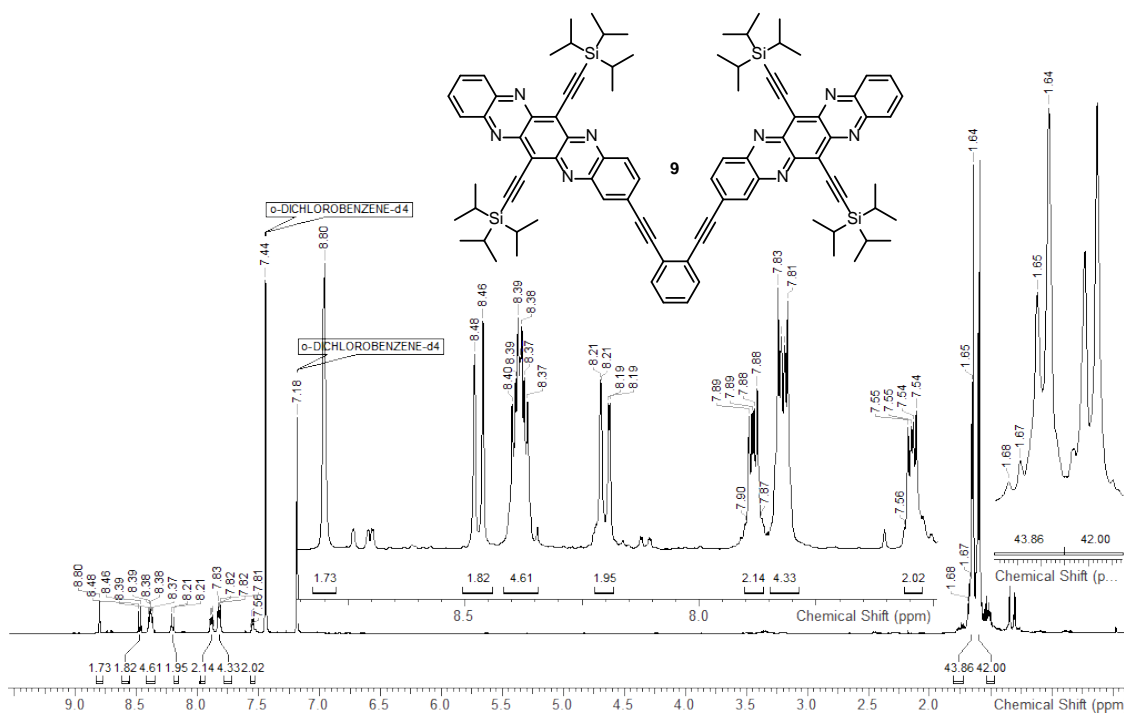


Figure S3.8: <sup>1</sup>H-NMR of 2D-construct 9.

Acquisition Time (sec)	1.7302	Date Stamp	08 Aug 2016 07:13:17	Frequency (MHz)	125.7578	Nucleus	<sup>13</sup> C
Number of Transients	8192	Original Points Count	65536	Points Count	65536	Receiver Gain	1620.00
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	13819.9316	SW (Hz)	37878.79	Sweep Width (Hz)	37878.21
Temperature (degree C)	22.010						

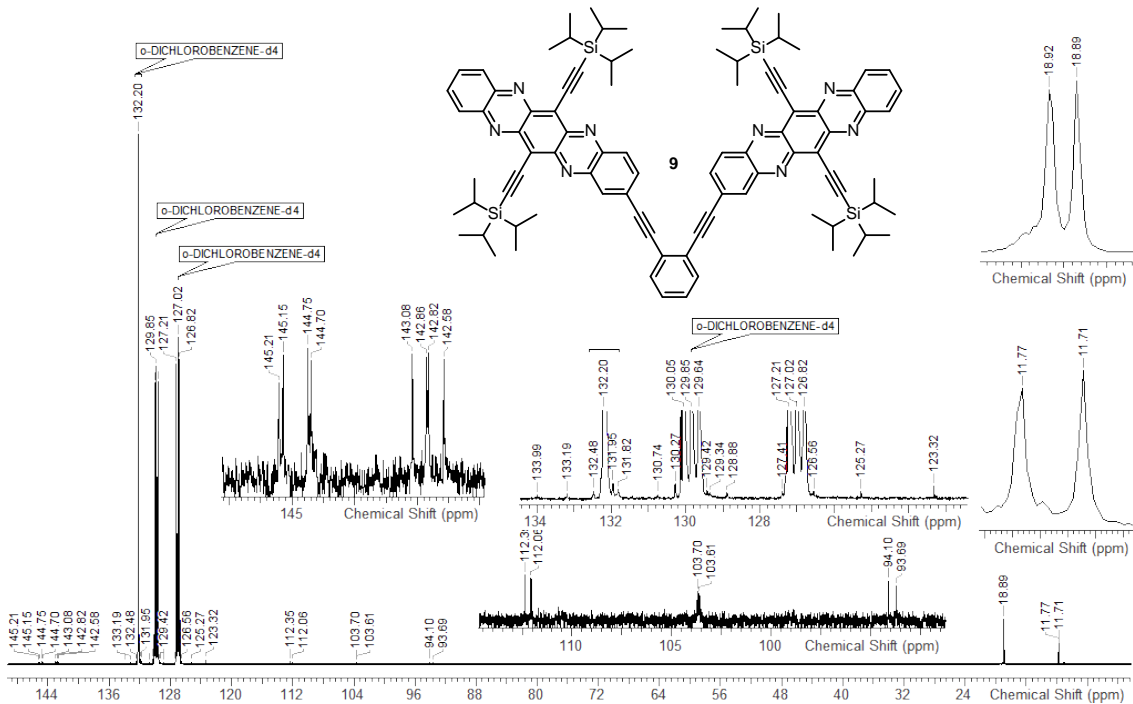


Figure S3.9: <sup>13</sup>C-NMR of construct 9.

Acquisition Time (sec)	3.6438	Date Stamp	09 Aug 2016 10:47:42	Frequency (MHz)	300.1301	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	32768	Points Count	32768	Receiver Gain	574.70
Solvent	o-C <sub>6</sub> D <sub>4</sub> O <sub>2</sub>	Spectrum Offset (Hz)	1498.4344	SW (Hz)	8992.81	Sweep Width (Hz)	8992.53
Temperature (degree C)	100.160						

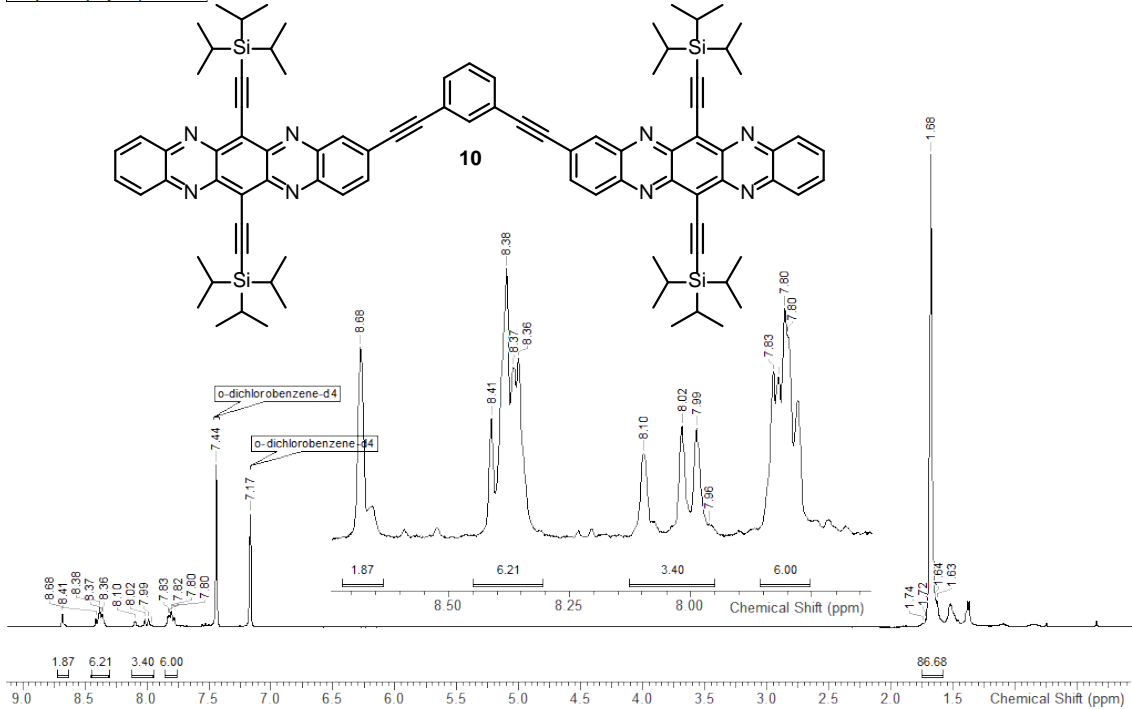


Figure S3.10: <sup>1</sup>H-NMR of construct 10.

Acquisition Time (sec)	1.7400	Date Stamp	10 Aug 2016 07:10:46	Frequency (MHz)	75.4678	Nucleus	<sup>13</sup> C
Number of Transients	10240	Original Points Count	32768	Points Count	65536	Receiver Gain	16384.00
Solvent	o-dichlorobenzene-d4	Spectrum Offset (Hz)	8261.4443	Sweep Width (Hz)	18832.11	Temperature (degree C)	100.160

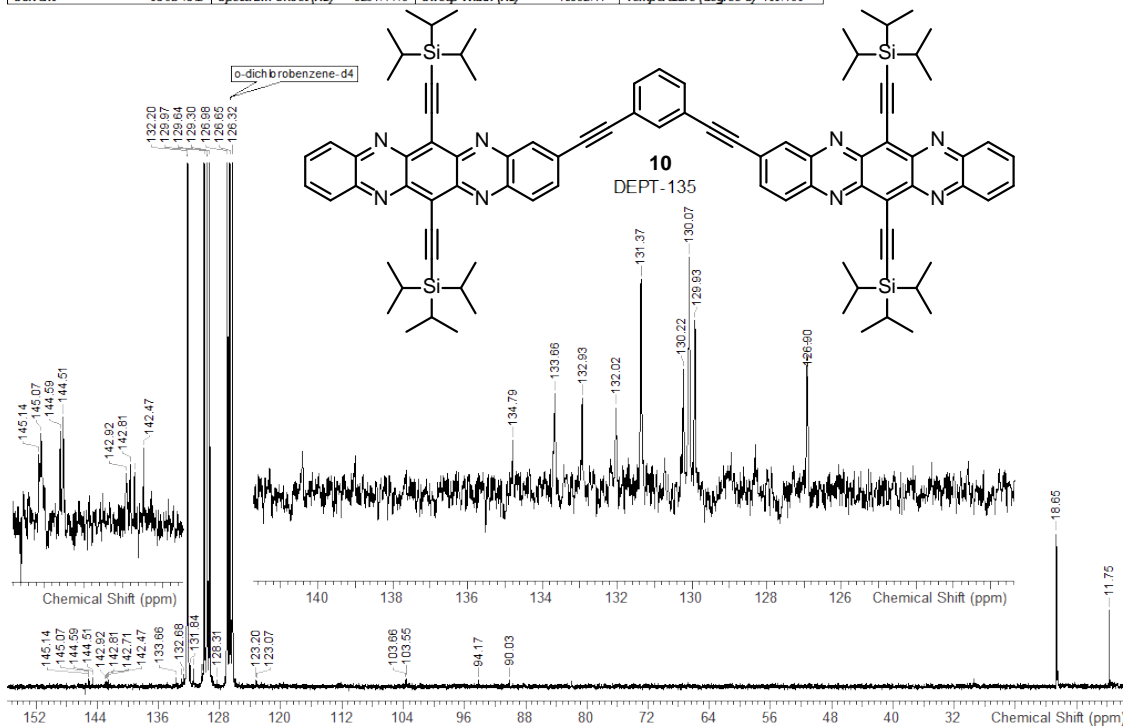


Figure S3.11: <sup>13</sup>C-NMR (DEPT-Inlet for aromatic CH-carbons) of 2D-construct 10.

Acquisition Time (sec)	3.6351	Date Stamp	19 Oct 2015 12:27:36	Frequency (MHz)	600.2438	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	65536	Points Count	65536	Receiver Gain	13.85
Solvent	THF	Spectrum Offset (Hz)	2807.8770	Sweep Width (Hz)	18028.57	Temperature (degree C)	22.002

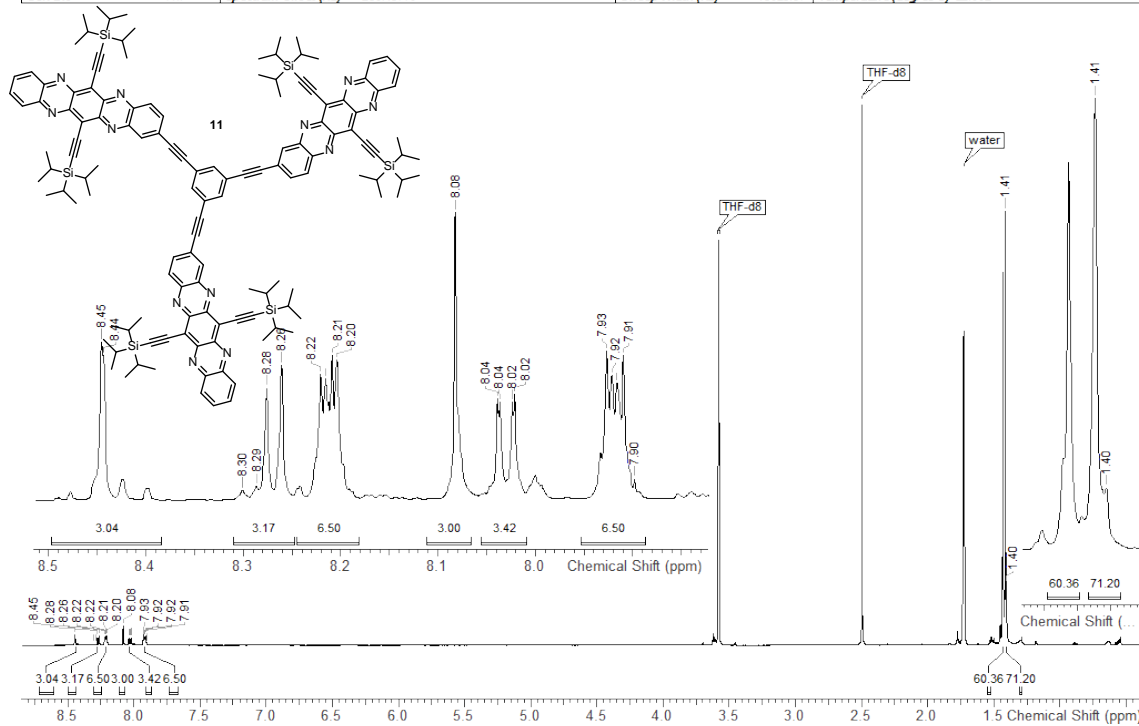


Figure S3.12: <sup>1</sup>H-NMR of 2D-construct 11.

Acquisition Time (sec)	1.0795	Date Stamp	19 Oct 2015 07:04:09	Frequency (MHz)	150.9314	Nucleus	<sup>13</sup> C
Number of Transients	6144	Original Points Count	49066	Points Count	65536	Receiver Gain	1290.00
Solvent	THF	Spectrum Offset (Hz)	16733.0098	Sweep Width (Hz)	45453.85	Temperature (degree C)	22.000

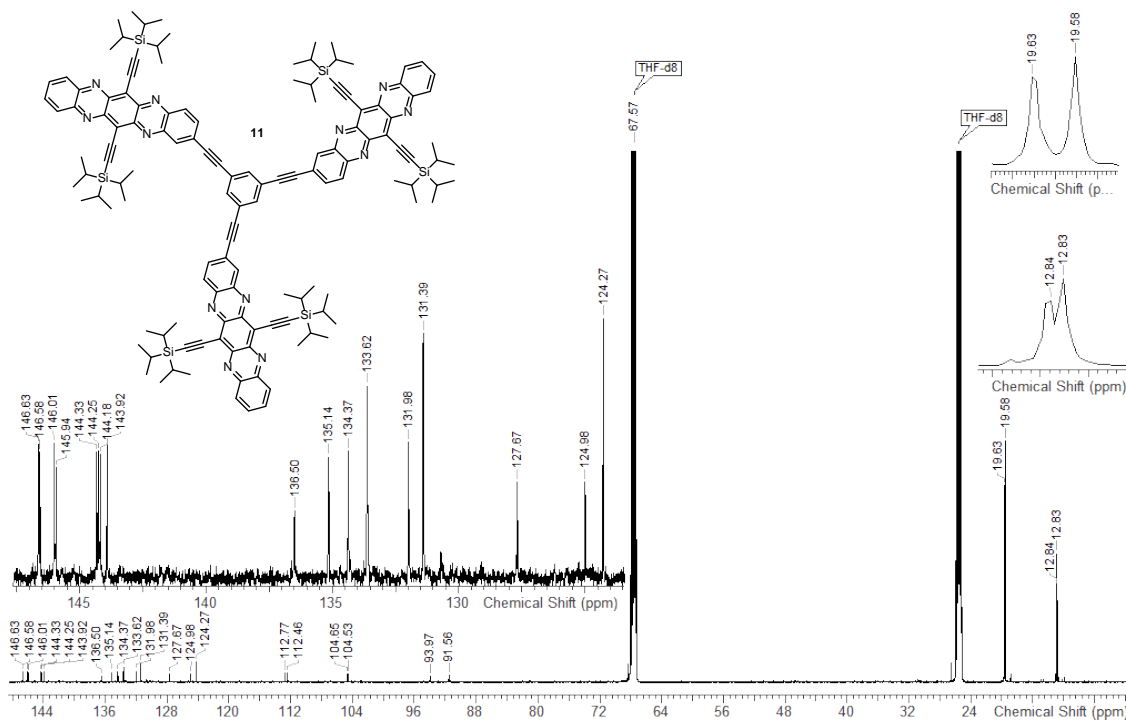


Figure S3.13: <sup>13</sup>C-NMR of 2D-construct 11.

Acquisition Time (sec)	3.6351	Date Stamp	19 Dec 2014 02:55:04	Frequency (MHz)	600.2438	Nucleus	<sup>1</sup> H
Number of Transients	128	Original Points Count	85536	Points Count	65536	Receiver Gain	15.35
Solvent	THF	Spectrum Offset (Hz)	4095.0754	Sweep Width (Hz)	18028.57	Temperature (degree C)	22.000

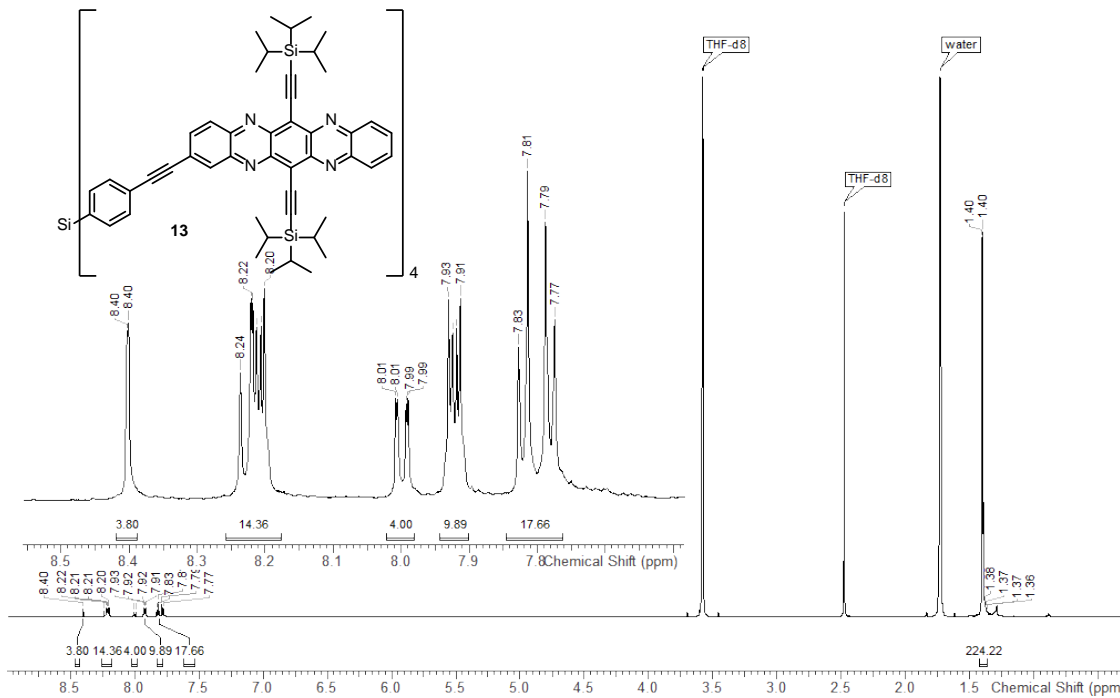


Figure S3.14: <sup>1</sup>H-NMR of 3D-construct 13.

Acquisition Time (sec)	1.0795	Date Stamp	18 Dec 2014 21:32:03	Frequency (MHz)	150.9314	Nucleus	<sup>13</sup> C
Number of Transients	6144	Original Points Count	49066	Points Count	65536	Receiver Gain	2050.00
Solvent	THF	Spectrum Offset (Hz)	17056.9102	Sweep Width (Hz)	45453.86	SW(cyclical) (Hz)	45454.55
						Temperature (degree C)	22.002

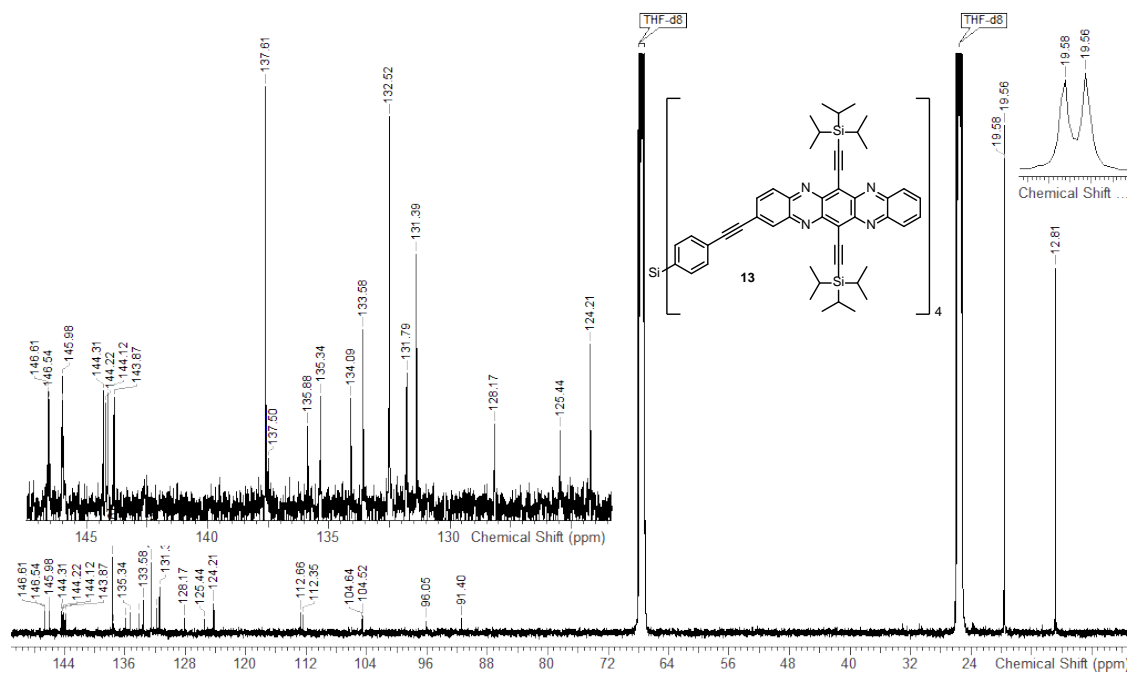


Figure S3.15: <sup>13</sup>C-NMR of 3D-construct 13.

## 4 IR-Spectroscopy

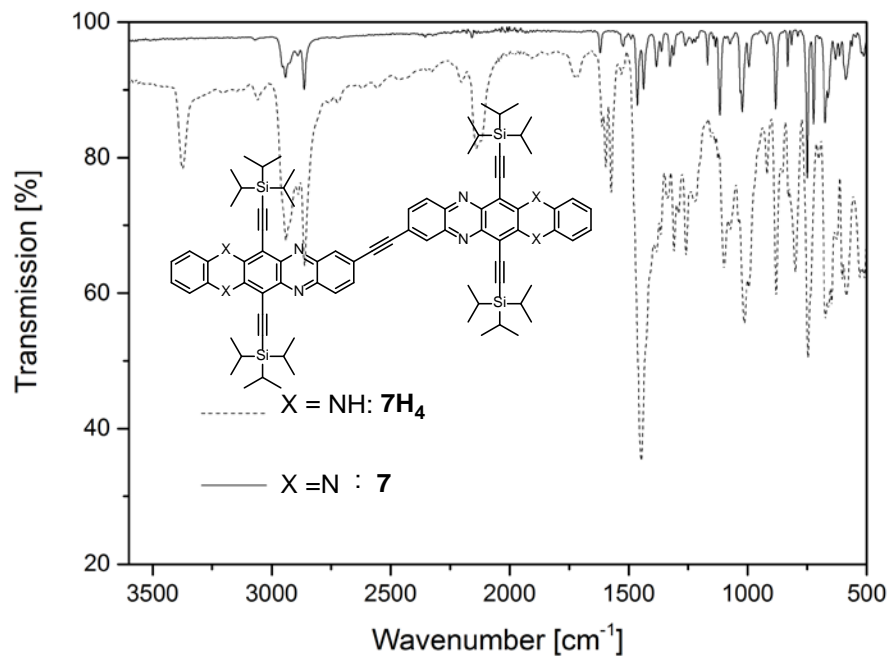


Figure S4.1: FT-IR of construct **7** and **7H<sub>4</sub>**.

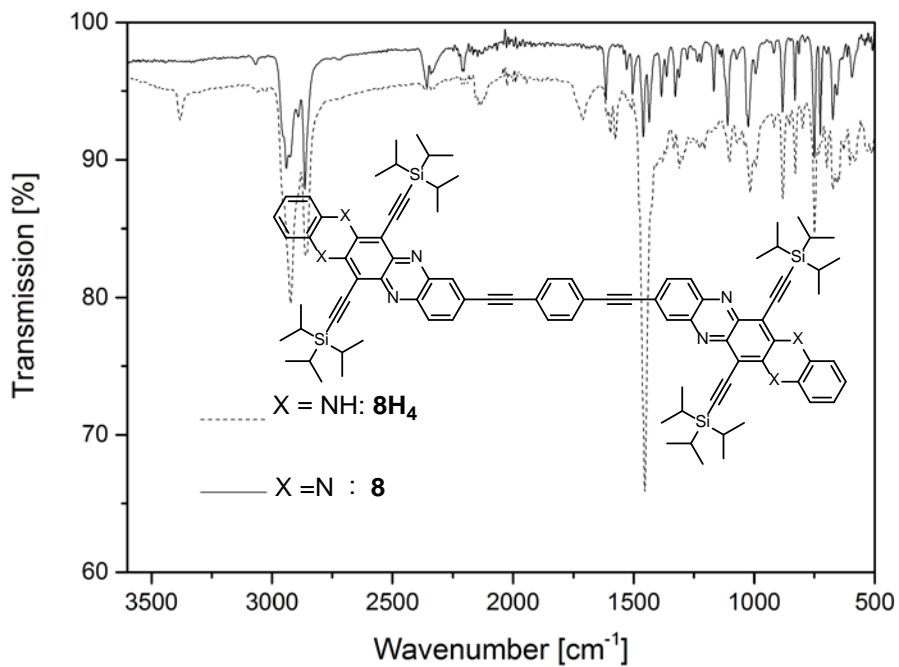
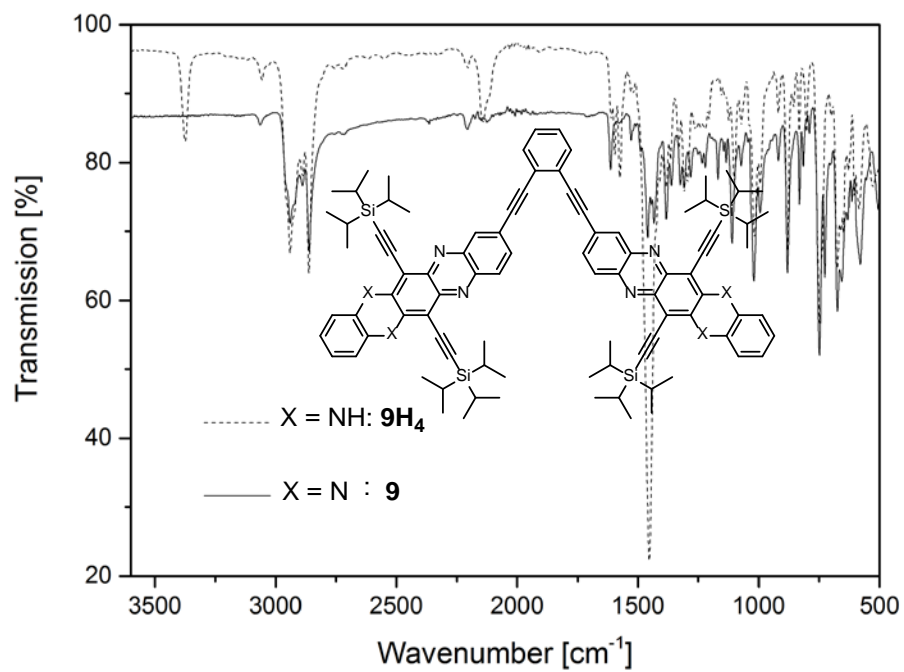
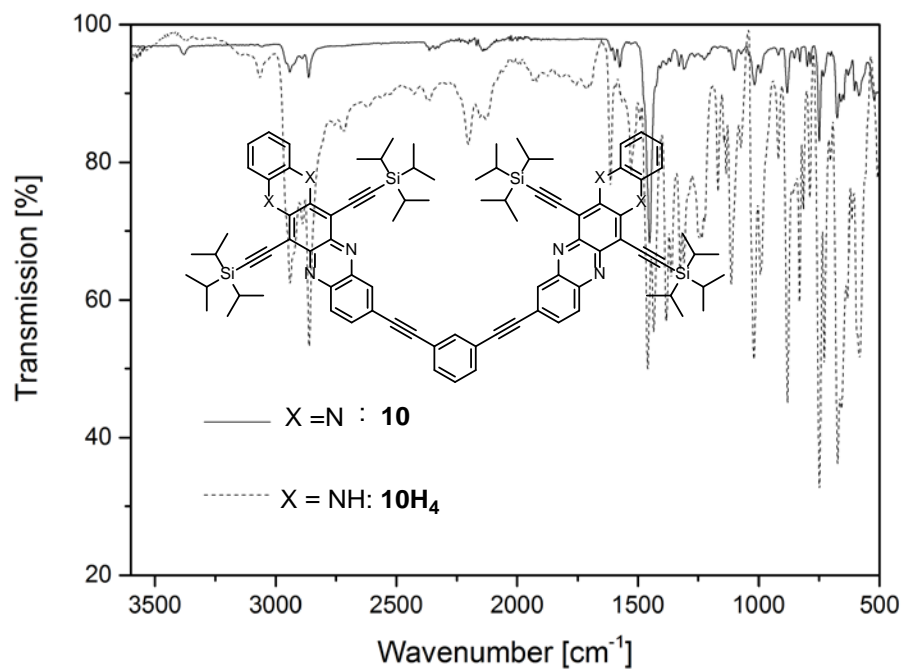


Figure S4.2: FT-IR of construct **8** and **8H<sub>4</sub>**.

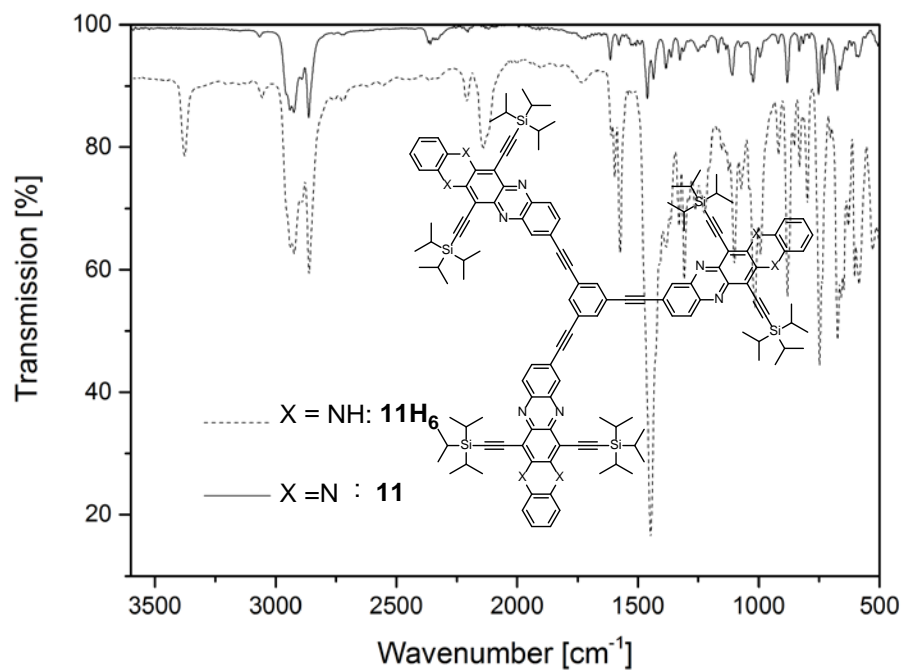




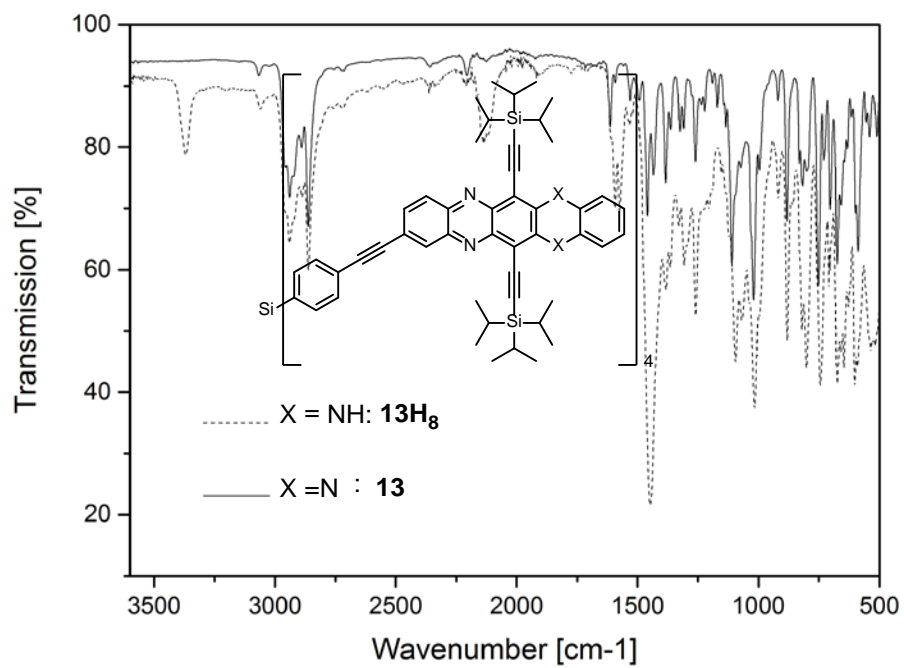
**Figure S4.3:** FT-IR of construct **9** and **9H<sub>4</sub>**.



**Figure S4.4:** FT-IR of construct **10** and **10H<sub>4</sub>**.

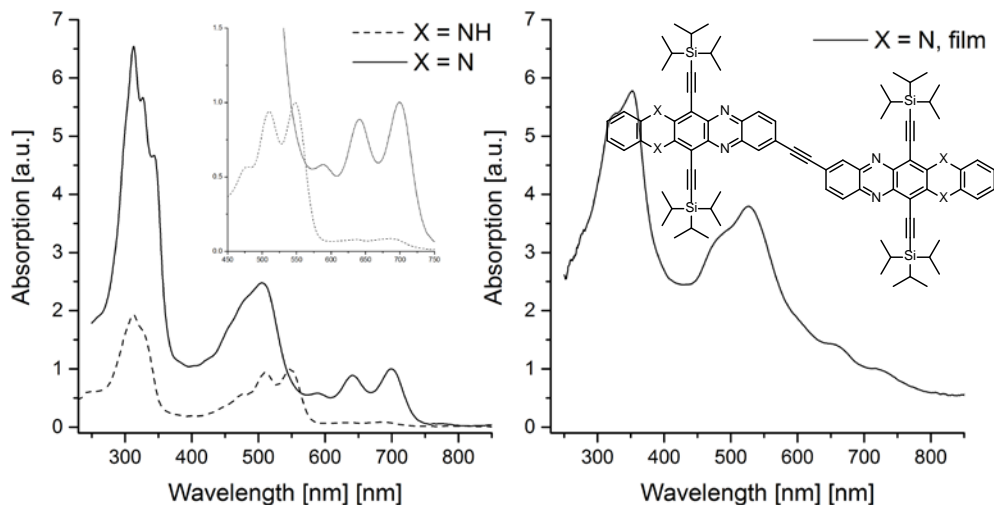


**Figure S4.5:** FT-IR of construct **11** and **11H<sub>4</sub>**.

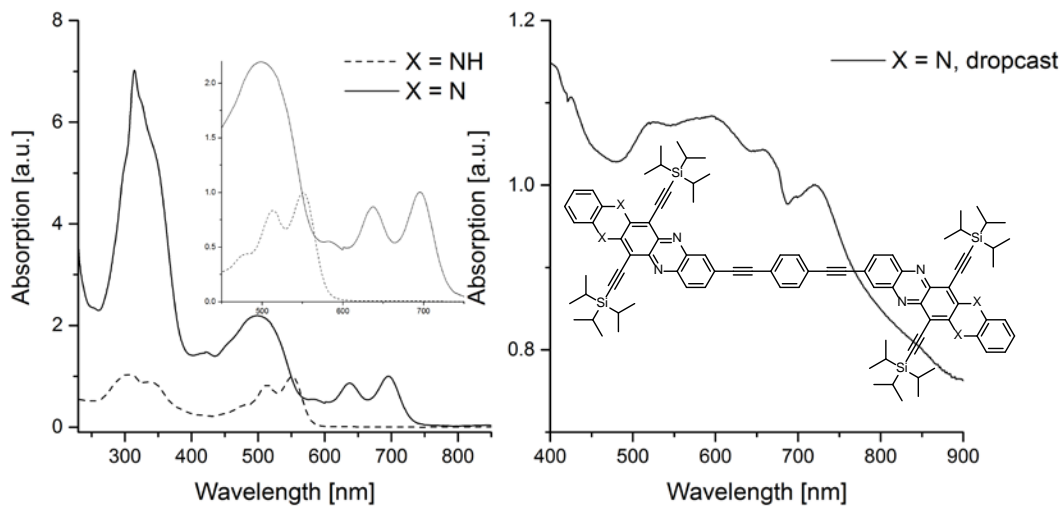


**Figure S4.6:** FT-IR of construct **13** and **13H<sub>4</sub>**.

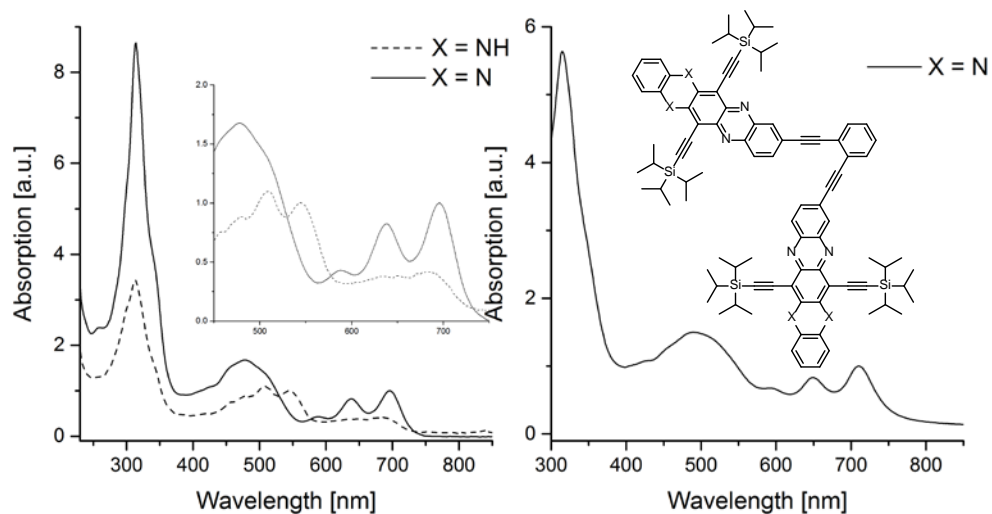
## 5 UVVis-Spectroscopy



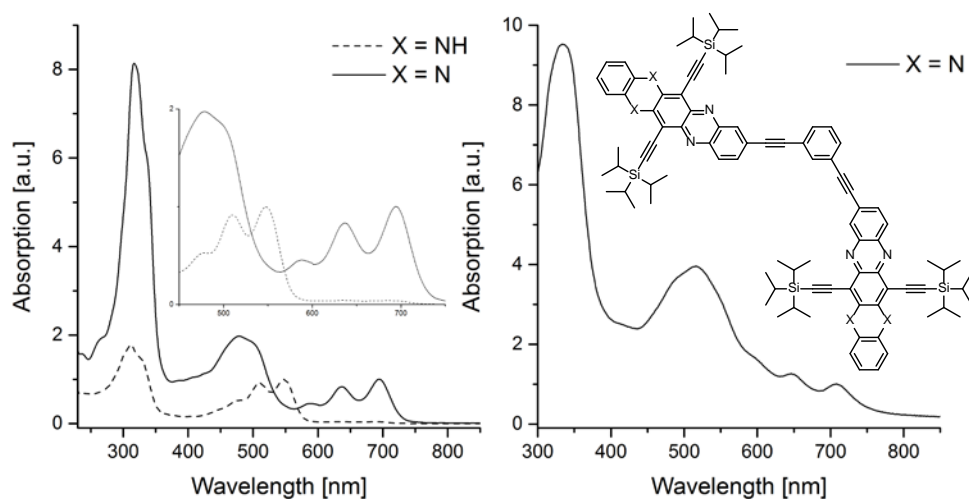
**Figure S5.1:** UVVis-spectra in solution (DCM) of **7** and **7H<sub>4</sub>** and of a film of **7** (spincoating, 1000 rpm, 1000 rpm/s, 20 s from 5 mg/mL toluene, 70 °C).



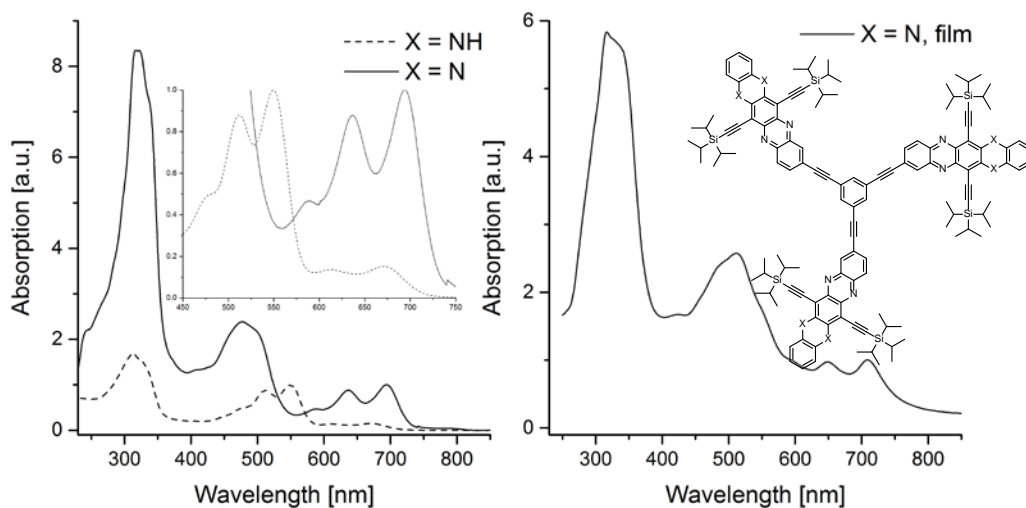
**Figure S5.2:** UVVis-spectra in solution (DCM) of **8** and **8H<sub>4</sub>** and of a film of **8** (dropcast from filtered CHCl<sub>3</sub> solution obtained from the oxidative aromatization, RT).



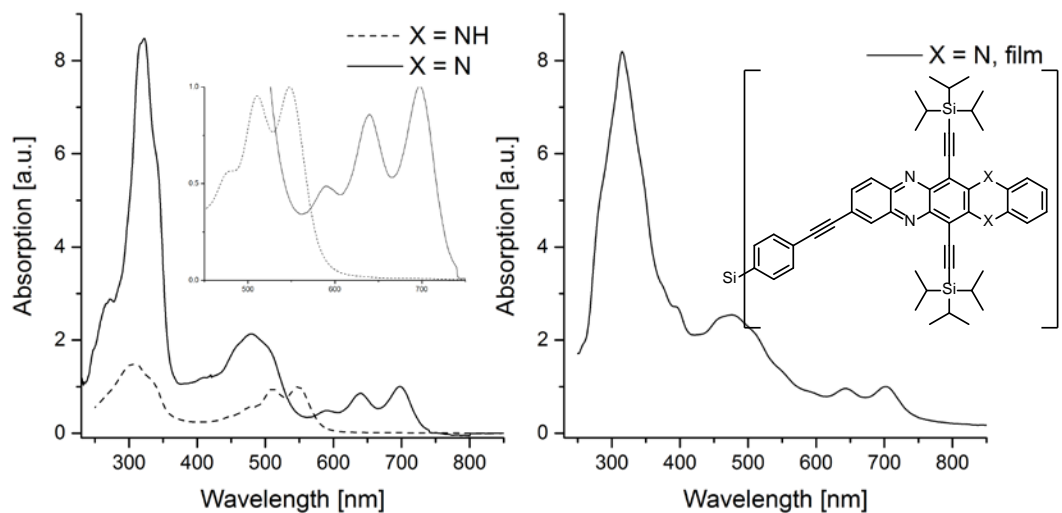
**Figure S5.3:** UVVis-spectra in solution (DCM) of **9** and **9H<sub>4</sub>** and of a film of **9** (spincoating, 10 mg/mL toluene, 600 rpm / 30 s, rt).



**Figure S5.4:** UVVis-spectra in solution (DCM) of **10** and **10H<sub>4</sub>** and of a film of **10** (spincoating, 10 mg/mL toluene, 600 rpm, 30 s, rt).



**Figure S5.5:** UVVis-spectra in solution (DCM) of **11** and **11H<sub>4</sub>** and of a film of **11** (spincoating, 1000 rpm, 1000 rpm/s, 20 s from 5 mg/mL toluene, rt).



**Figure S5.6:** UVVis-spectra in solution (DCM) of **13** and **13H<sub>4</sub>** and of a film of **13** (spincoating, 1000 rpm, 1000 rpm/s, 20 s from 5 mg/mL toluene, rt).

## 6 Cyclic Voltammetry

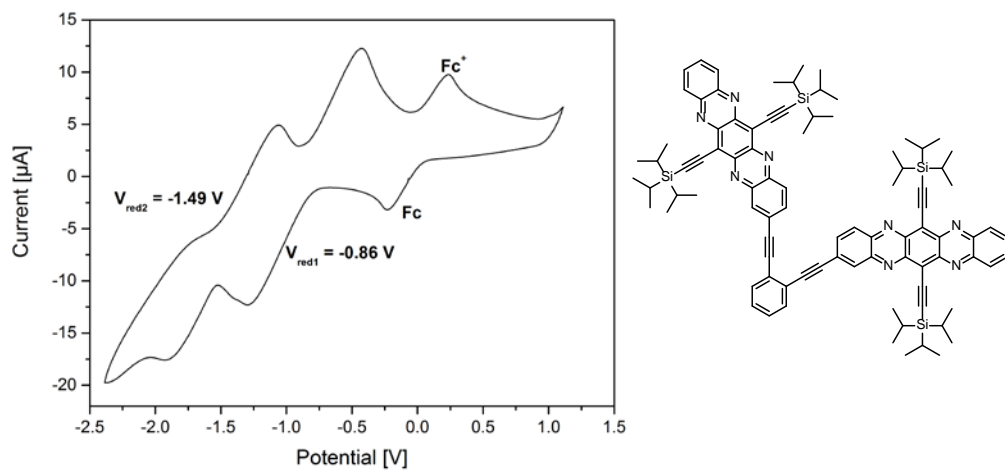


Figure S6.1: CV of **9**.

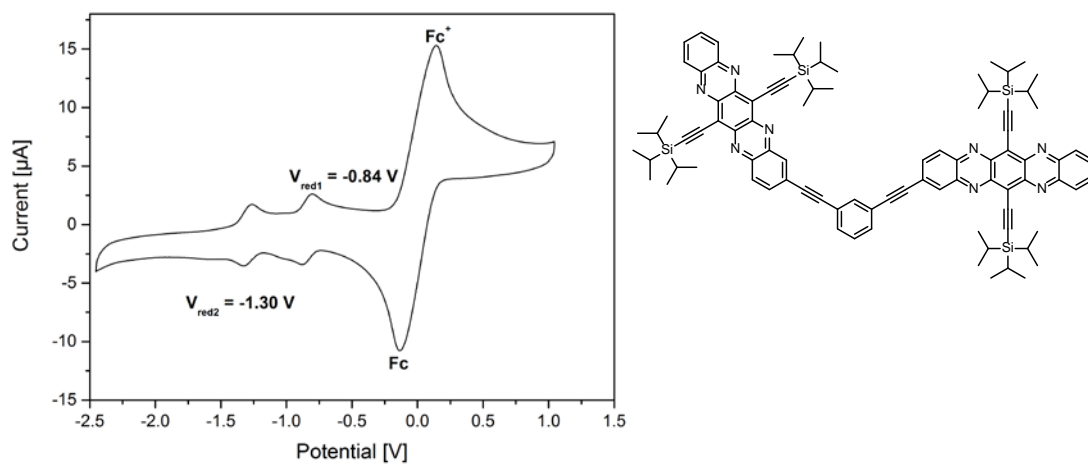


Figure S6.2: CV of **10**.

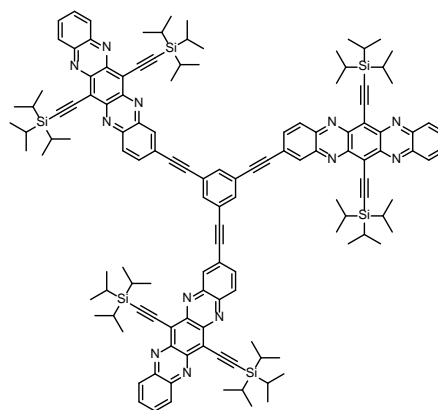
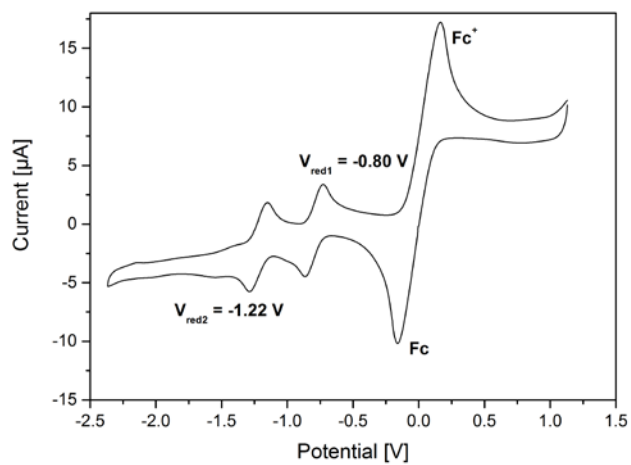


Figure S6.3: CV of 11.

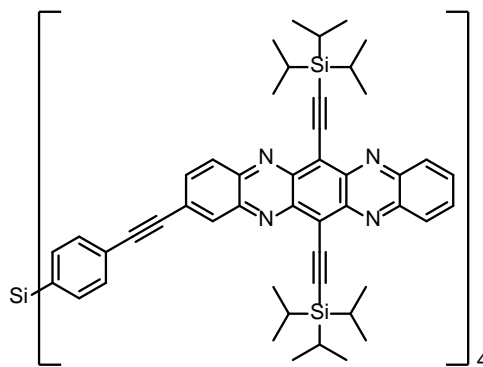
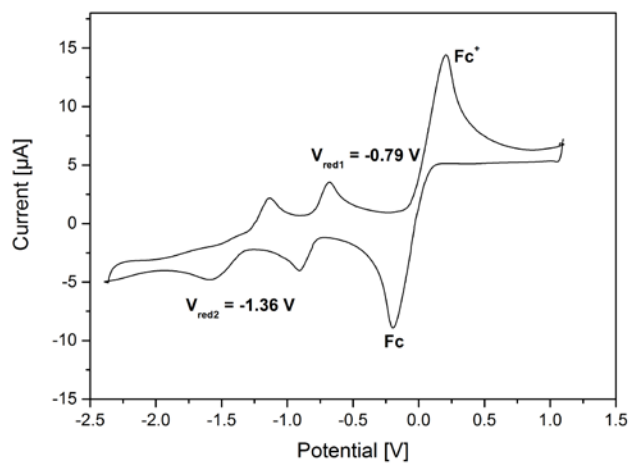
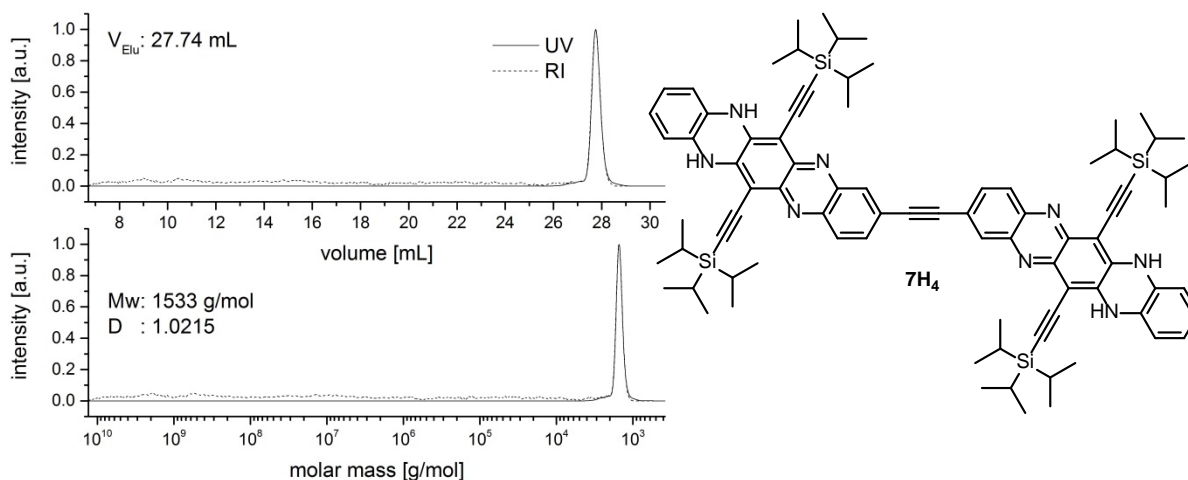


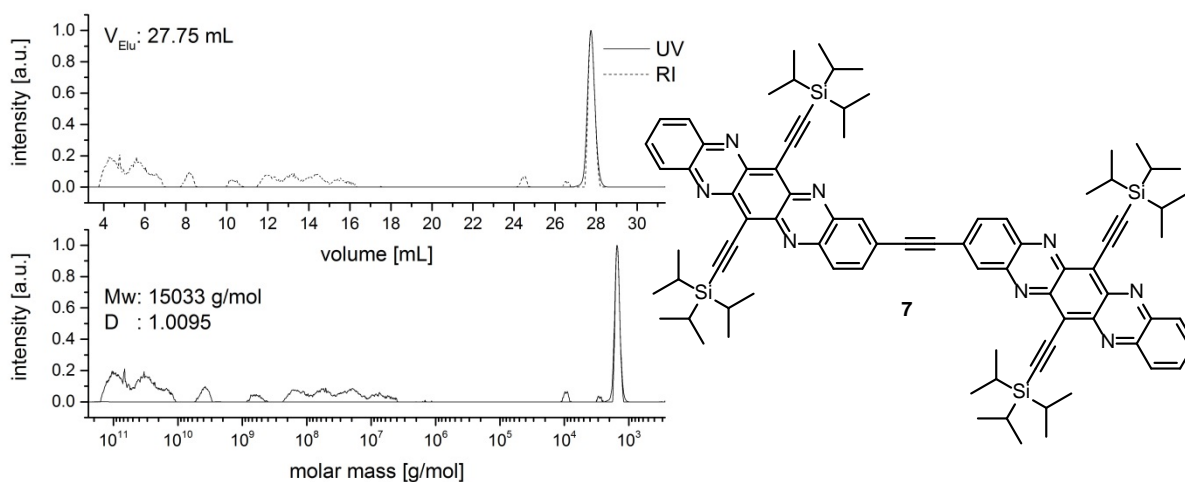
Figure S6.4: CV of 13.

## 7 Analytical Gel Permeation Chromatography

Reaction controls and purity control were performed by analytical GPC.

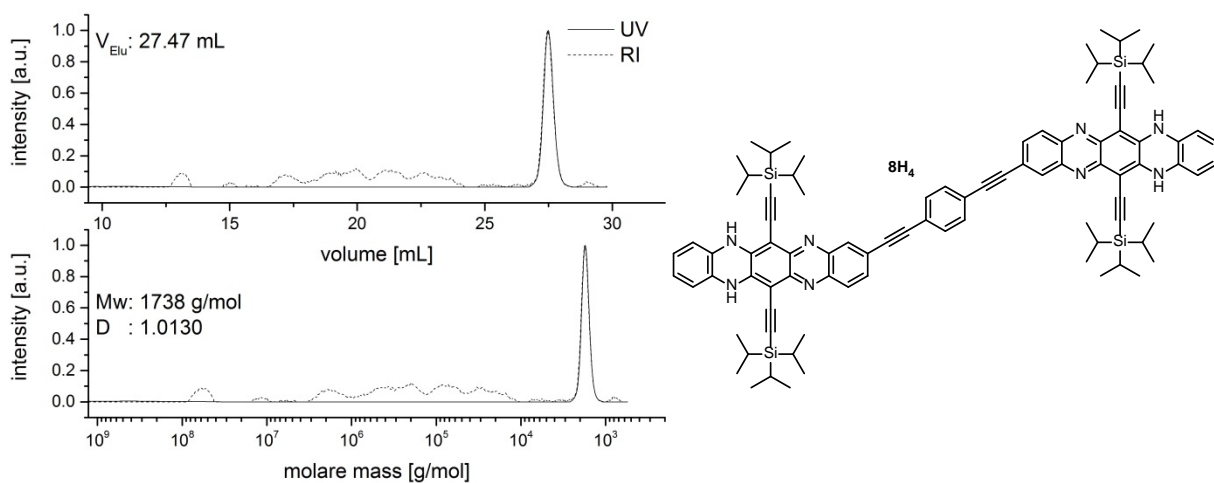


**Figure S7.1:** Normalized GPC-traces of purified construct **7H<sub>4</sub>** (only one tautomer depicted).

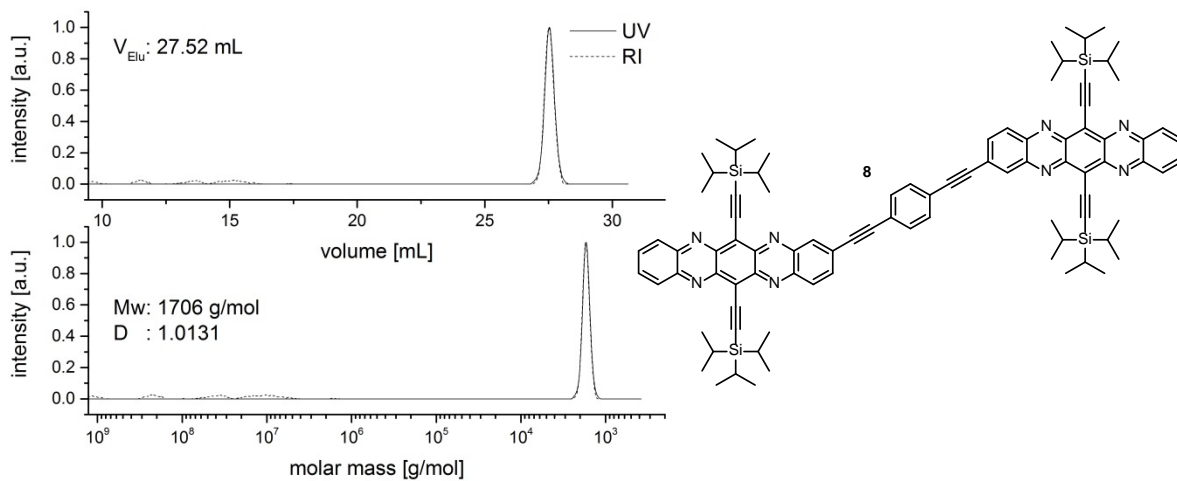


**Figure S7.2:** Normalized GPC-traces of purified construct **7** (noise in RI-trace due to weak detector signal).

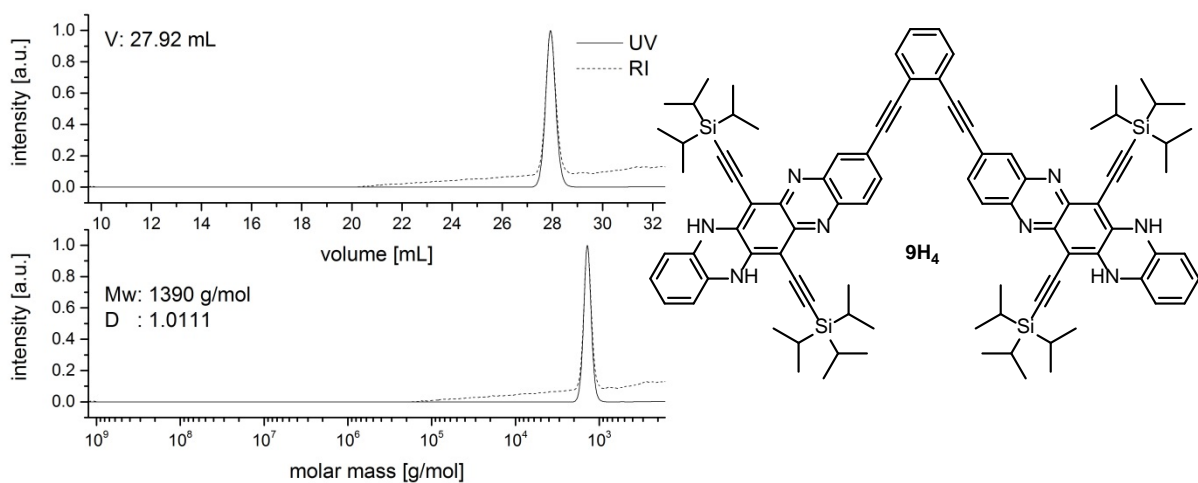




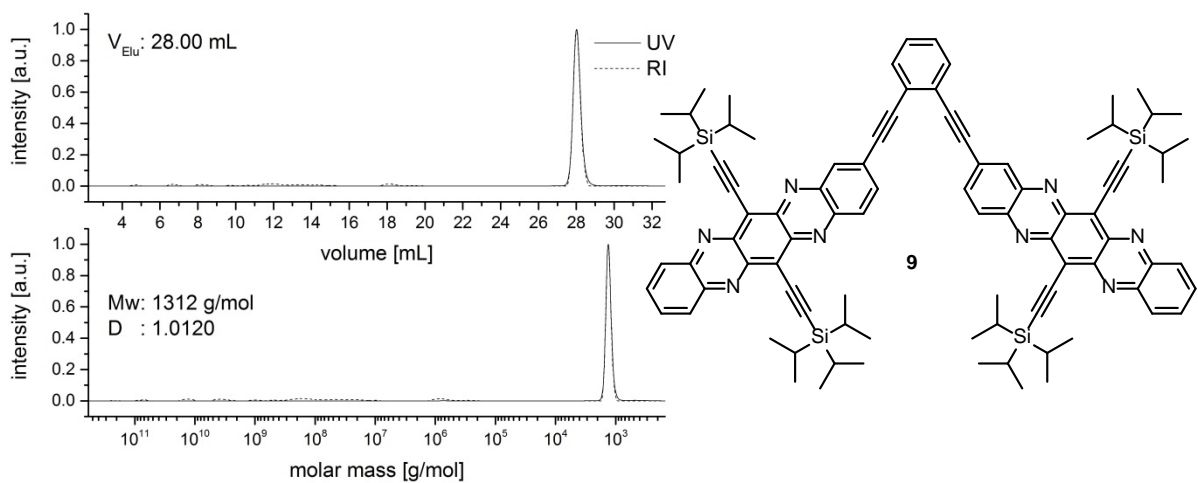
**Figure S7.3:** Normalized GPC-traces of purified construct **8H<sub>4</sub>** (noise in RI-trace due to weak detector signal).



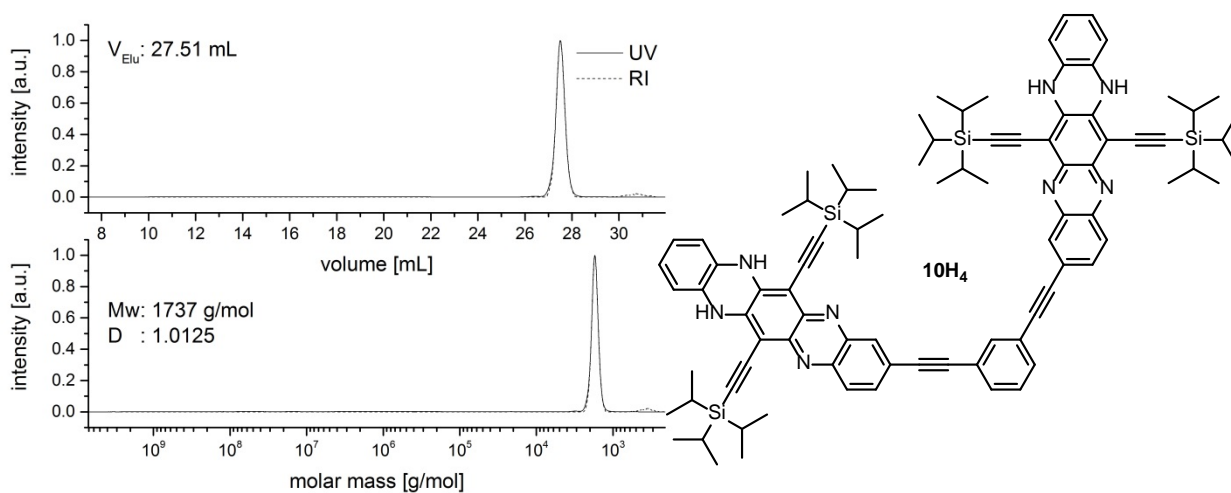
**Figure S7.4:** Normalized GPC-traces of purified construct **8** (noise in RI-trace due to weak detector signal).



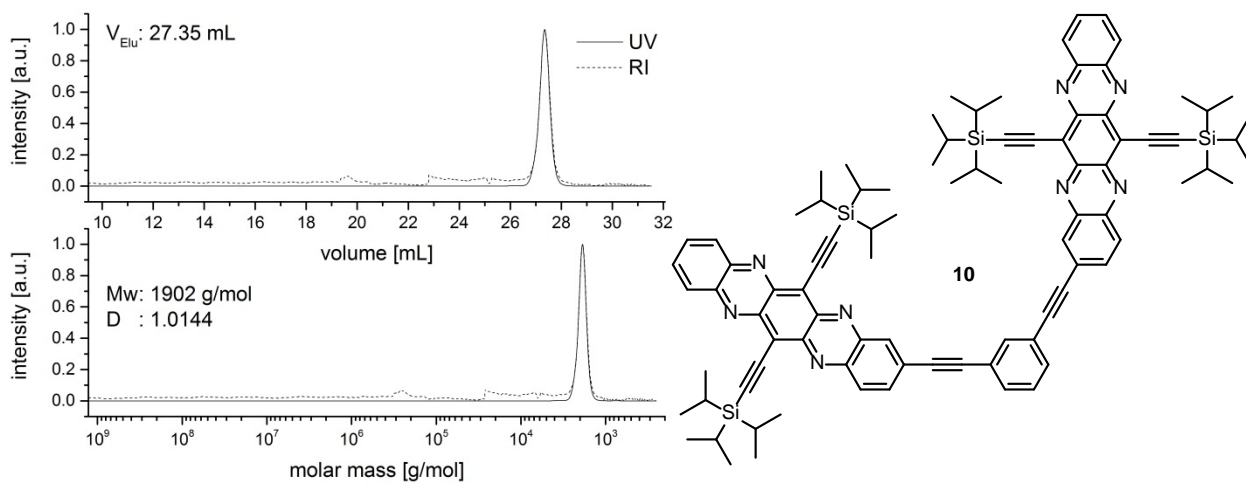
**Figure S7.5:** Normalized GPC-traces of purified construct **9**.



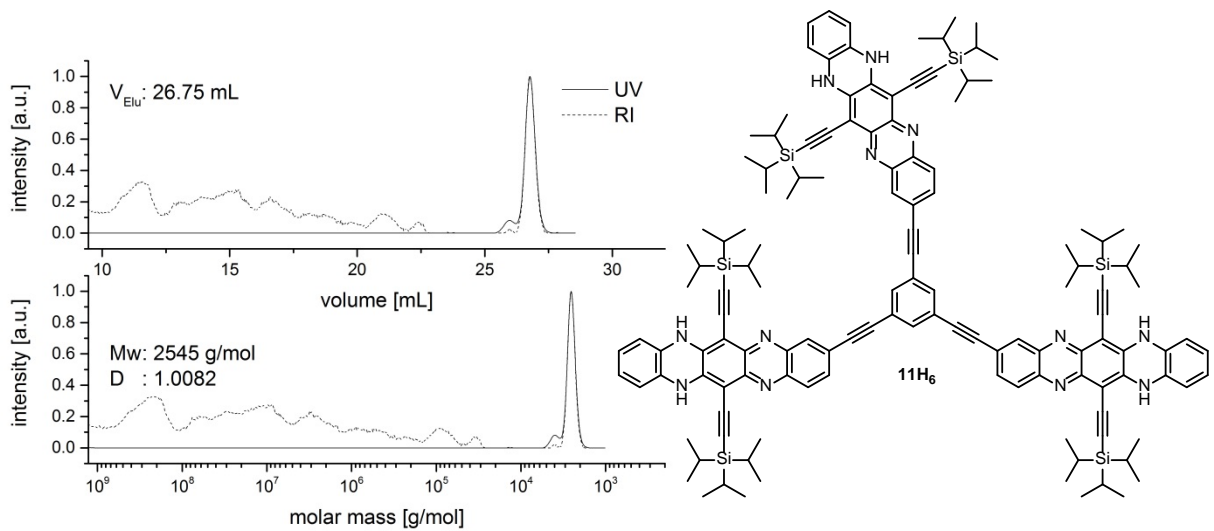
**Figure S7.6:** Normalized GPC-traces of purified construct **9**.



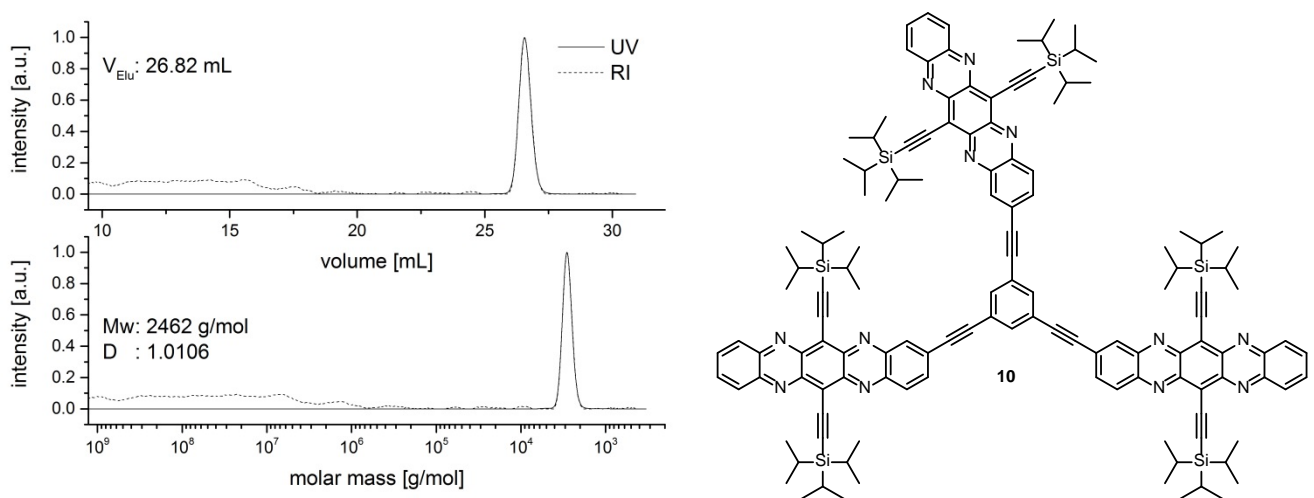
**Figure S7.7:** Normalized GPC-traces of purified construct **10H<sub>4</sub>**.



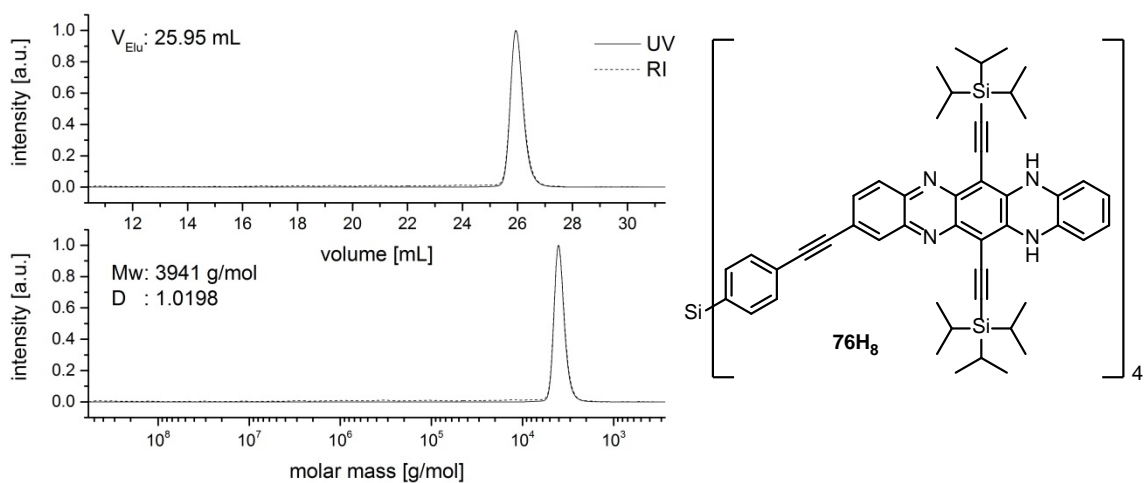
**Figure S7.8:** Normalized GPC-traces of purified construct **10** (noise in RI-trace due to weak detector signal).



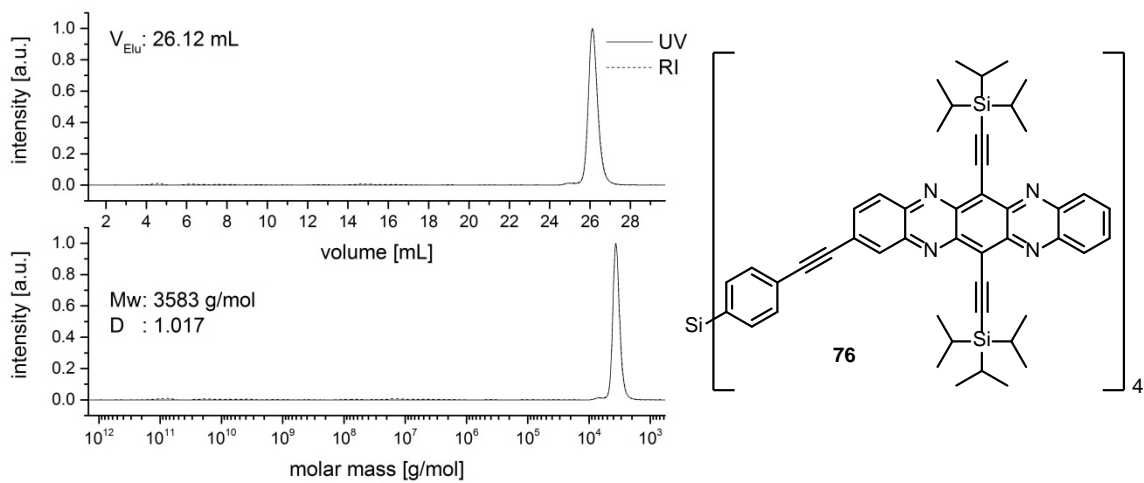
**Figure S7.9:** Normalized GPC-traces of purified construct **11H<sub>6</sub>** (noise in RI-trace due to weak detector signal).



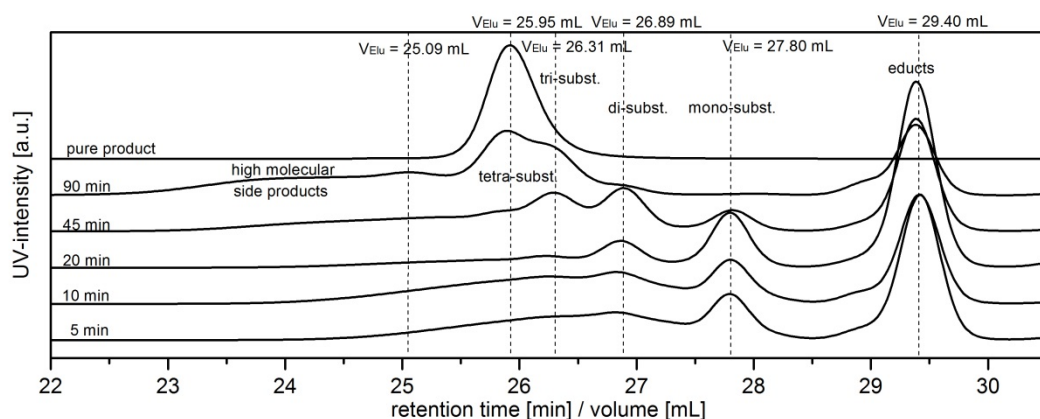
**Figure S7.10:** Normalized GPC-traces of purified construct **11**.



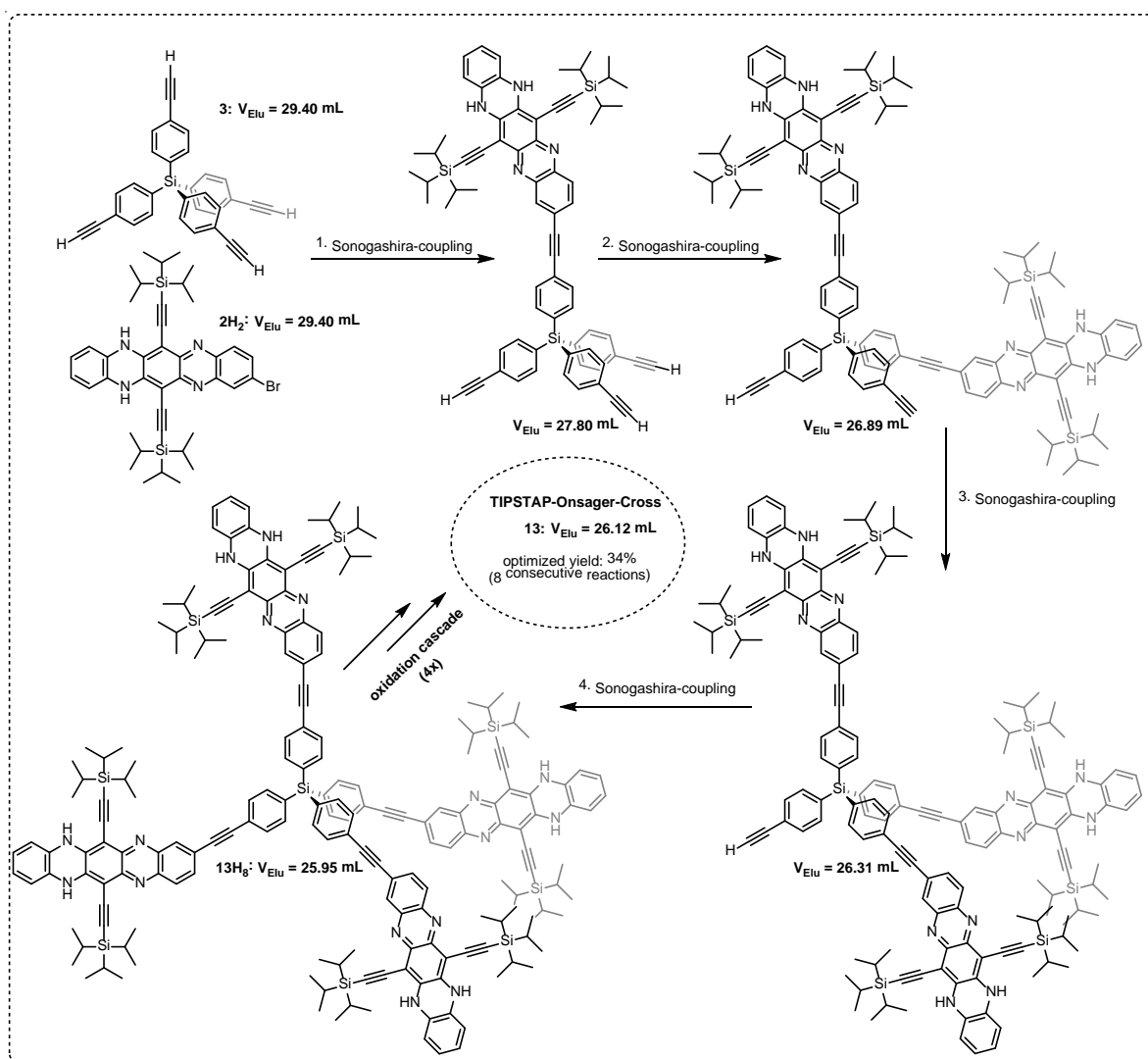
**Figure S7.11:** Normalized GPC-traces of purified construct **13H<sub>6</sub>**.



**Figure S7.12:** Normalized GPC-traces of purified construct **13**.



**Figure S7.13:** UV-traces of analytical GPC measurements of the cross coupling from **3** with **2H<sub>2</sub>** to **13H<sub>8</sub>**. Samples were freed from catalyst residue by passing through a short silica filled pipette (THF). Tight observation of the coupling cascade by GPC ensures the best yields.



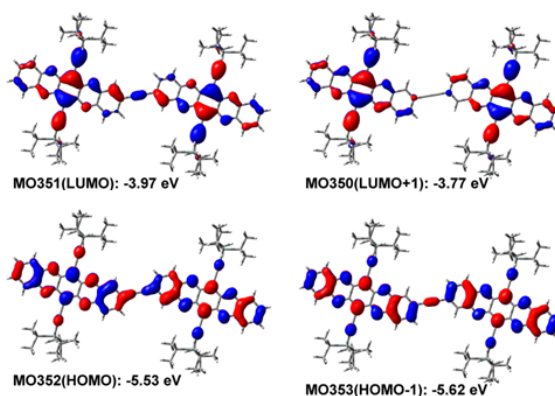
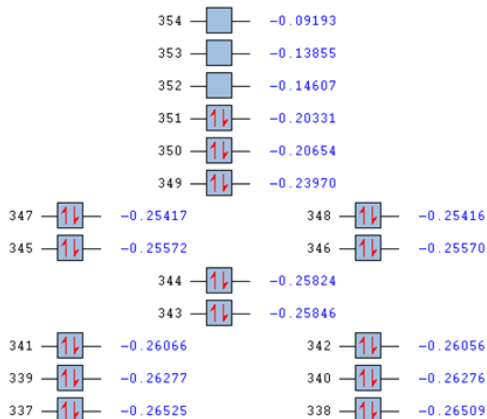
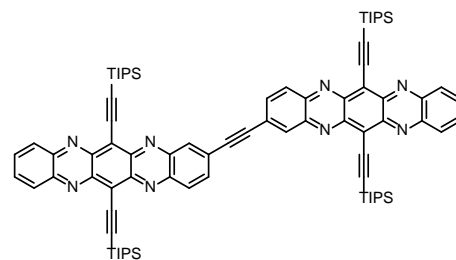
**Figure S7.14:** Chemical structures and elution volumes of intermediated in the coupling cascade towards Onsager cross **13H<sub>8</sub>**.

## 8 Computational Chemistry

For quantum chemical calculations, a cluster computer (12 knots, 12 CPU cores, 24 GB RAM and 500 GB hard drive) was used. Spartan 10 (Wavefunction Inc.) was used to generate MM2-optimized structures that were exported to TURBOMOLE-6.3.1. The structures were geometry optimized (DFT, BP86), the geometry refined (DFT, BP86-def2-TZVP). The below depicted energies and orbital schemes were calculated by a DFT-single point energy calculation (previously optimized geometry exported to GAUSSIAN and the electronic structure was optimized without further geometry refinements). For this, B3LYP-6311Gdp was used.

### TIPS-TAP dimer 7

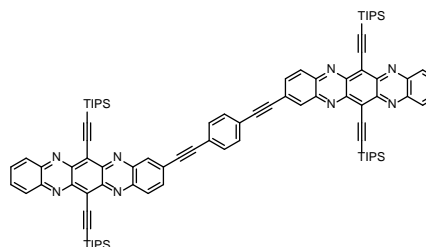
basis set	orbital	Hartree	eV
6-311Gdp	MO 350 (HOMO-1):	-0.20654	-5.62
	MO 351 (HOMO):	-0.20331	-5.53
	MO 352 (LUMO):	-0.14607	-3.97
	MO 353 (LUMO+1):	-0.13855	-3.77

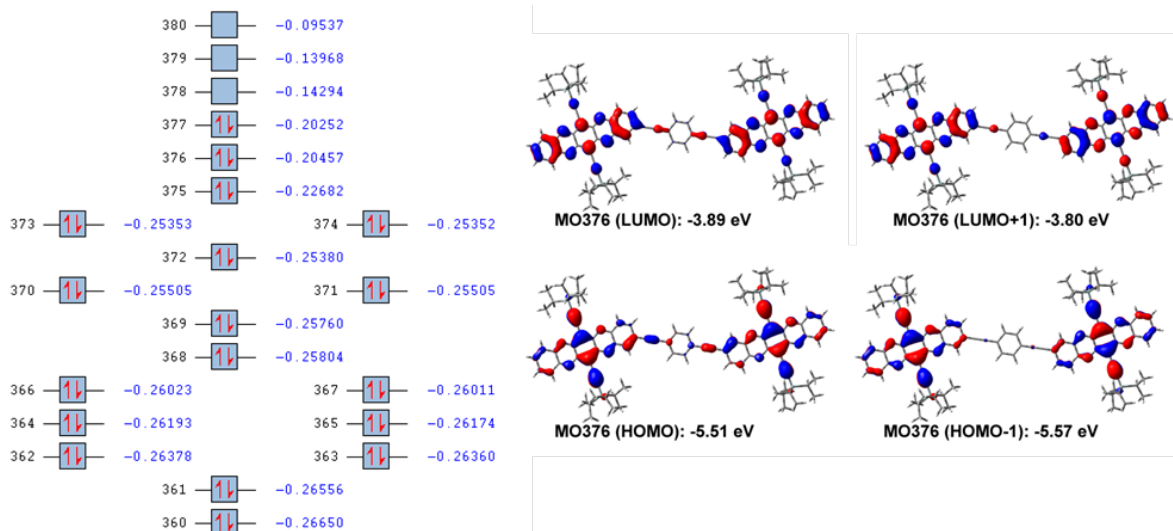


**Figure S8.1:** (Partial) MO-scheme of **7** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0002 Hartree. Graphical representation of the relevant MOs.

### TIPSTAP dimer 8

basis set	orbital	Hartree	eV
6-311Gdp	MO 376 (HOMO-1):	-0.20457	-5.57
	MO 377 (HOMO):	-0.20252	-5.51
	MO 378 (LUMO):	-0.14294	-3.89
	MO 379 (LUMO+1):	-0.13968	-3.80

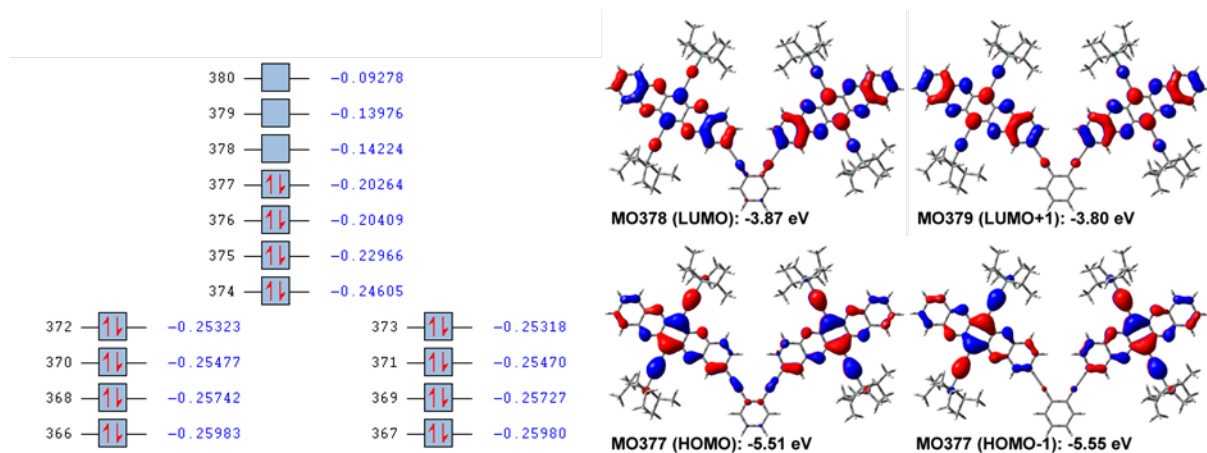
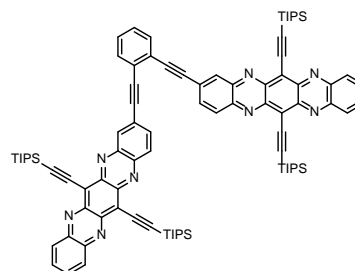




**Figure S8.2:** (Partial) MO-scheme of **8** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0002 Hartree. Graphical representation of the relevant MOs.

### TIPS-TAP Dimer 9

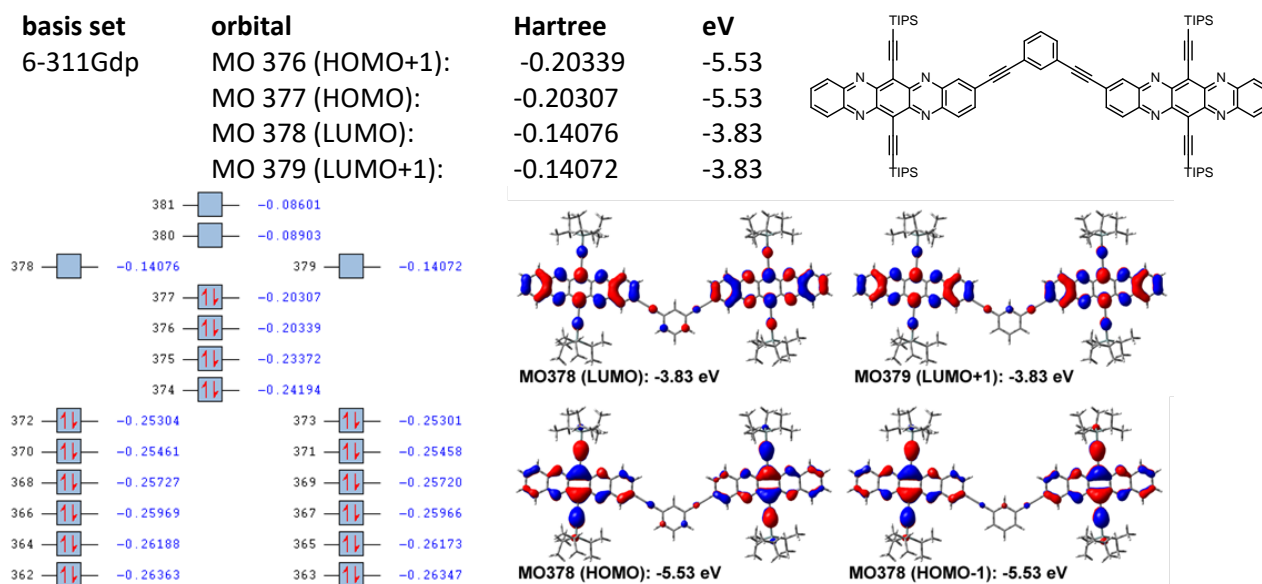
basis set	orbital	Hartree	eV
6-311Gdp	MO 376 (HOMO-1):	-0.20409	-5.55
	MO 377 (HOMO):	-0.20264	-5.51
	MO 378 (LUMO):	-0.14224	-3.87
	MO 379 (LUMO+1):	-0.13976	-3.80



**Figure S8.3:** (Partial) MO-scheme of **9** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0002 Hartree. Graphical representation of the relevant MOs.

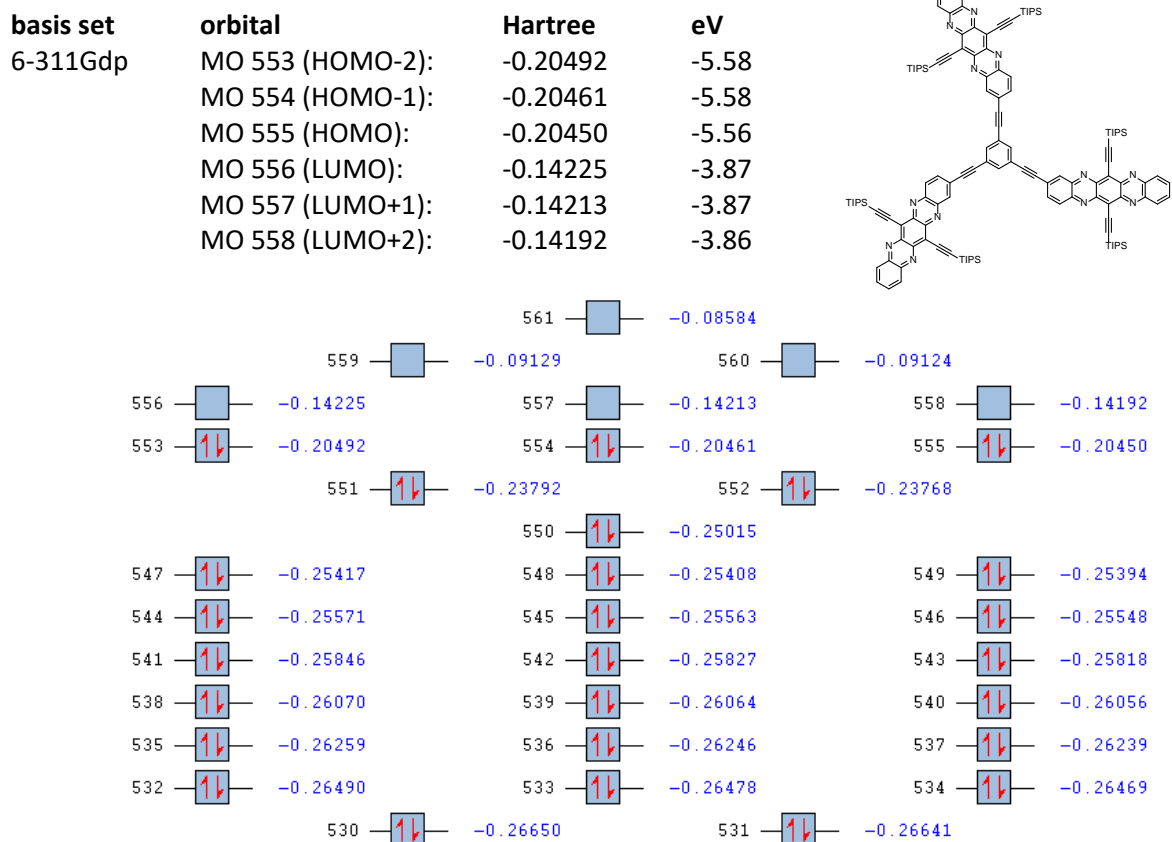


### TIPSTAP dimer 10



**Figure S8.4:** (Partial) MO-scheme of **8** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0002 Hartree. Graphical representation of the relevant MOs.

### TIPSTAP trimer 11



**Figure S8.5:** (Partial) MO-scheme of **11** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0004 Hartree.

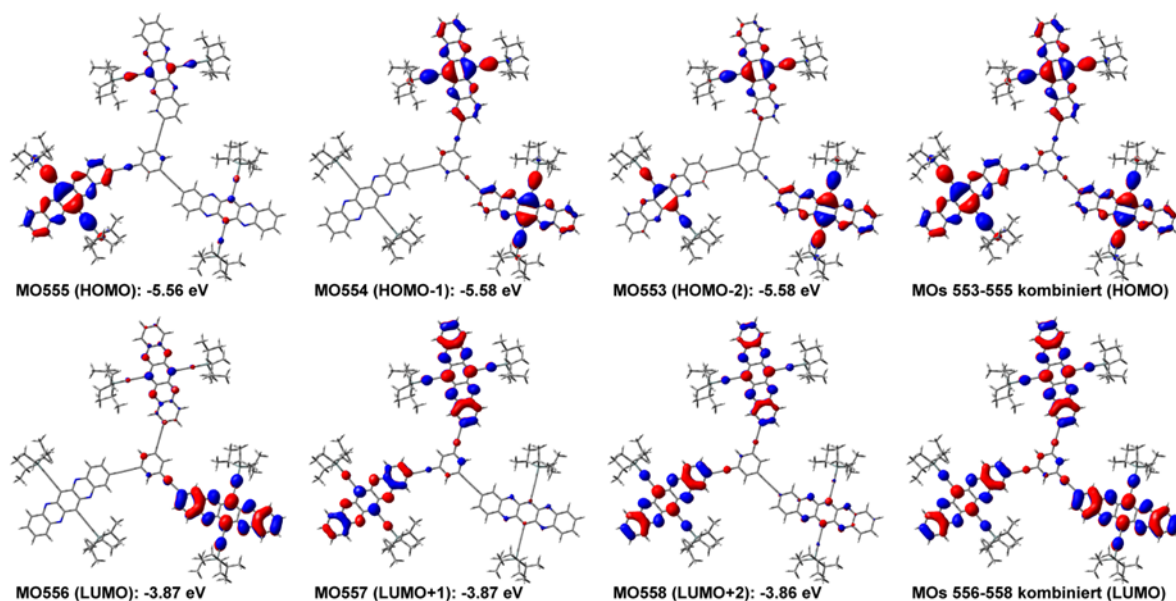


Figure S8.6: Graphical representation of the relevant MOs of **11**.

### TIPSTAP Onsager-cross **13**

basis set	orbital	Hartree	eV
6-311Gdp	MO 798 (HOMO-3):	-0.20389	-5.55
	MO 799 (HOMO-2):	-0.20357	-5.54
	MO 800 (HOMO-1):	-0.20337	-5.53
	MO 801 (HOMO):	-0.20330	-5.53
	MO 802 (LUMO):	-0.14194	-3.86
	MO 803 (LUMO+1):	-0.14167	-3.86
	MO 804 (LUMO+2):	-0.14162	-3.85
	MO 805 (LUMO+3):	-0.14150	-3.85

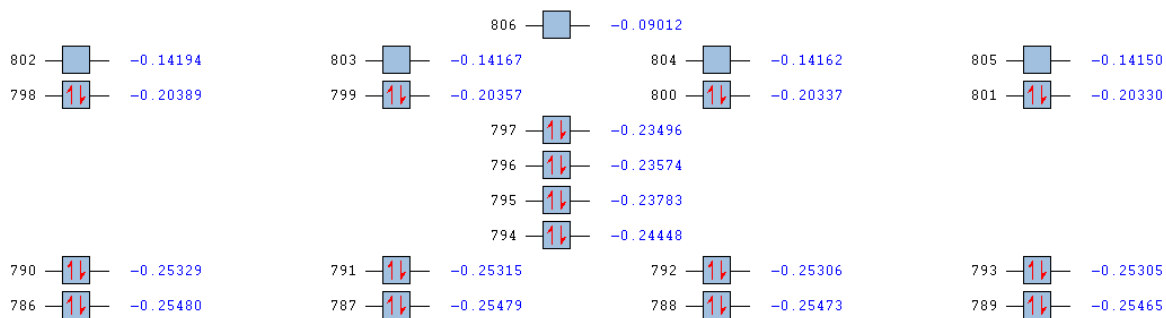
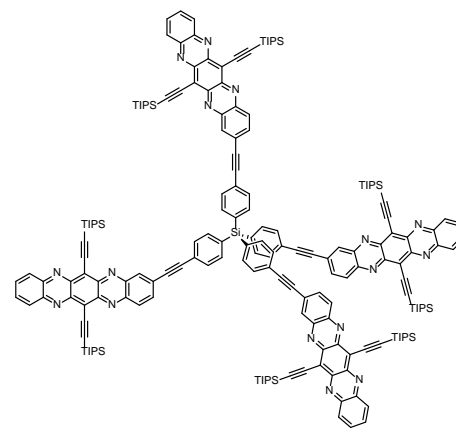
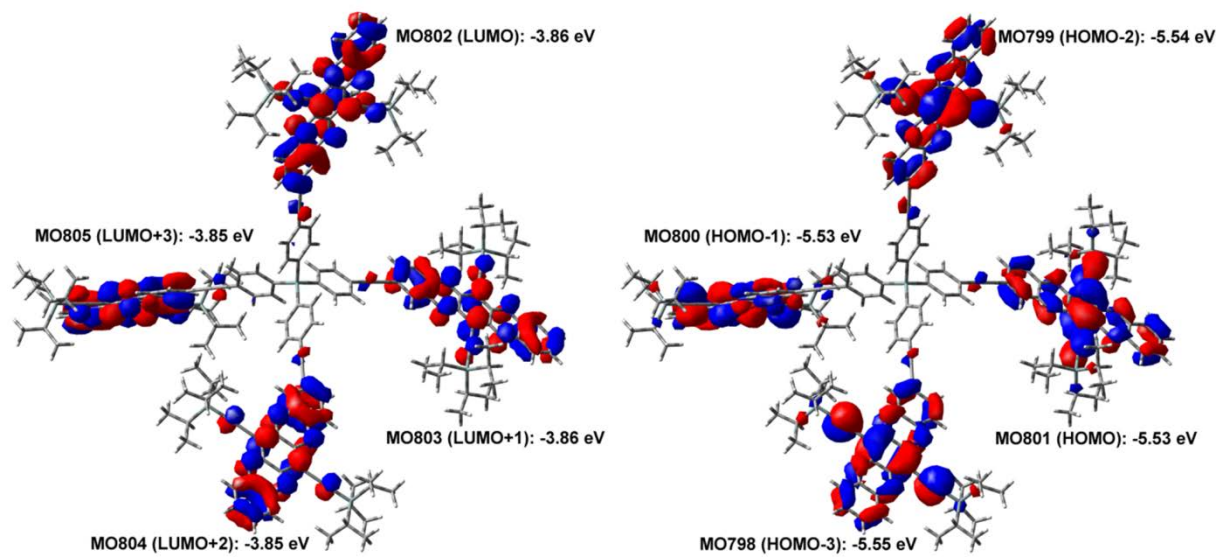


Figure S8.7: (Partial) MO-scheme of **13** (B3LYP 6-311Gdp). Energies in Hartree. Degeneracy threshold at 0.0004 Hartree.



**Figure S8.8:** Graphical representation of the relevant MOs of **13**.

# 9 XP- and UP-Spectroscopy

## 9.1 1D-construct 7

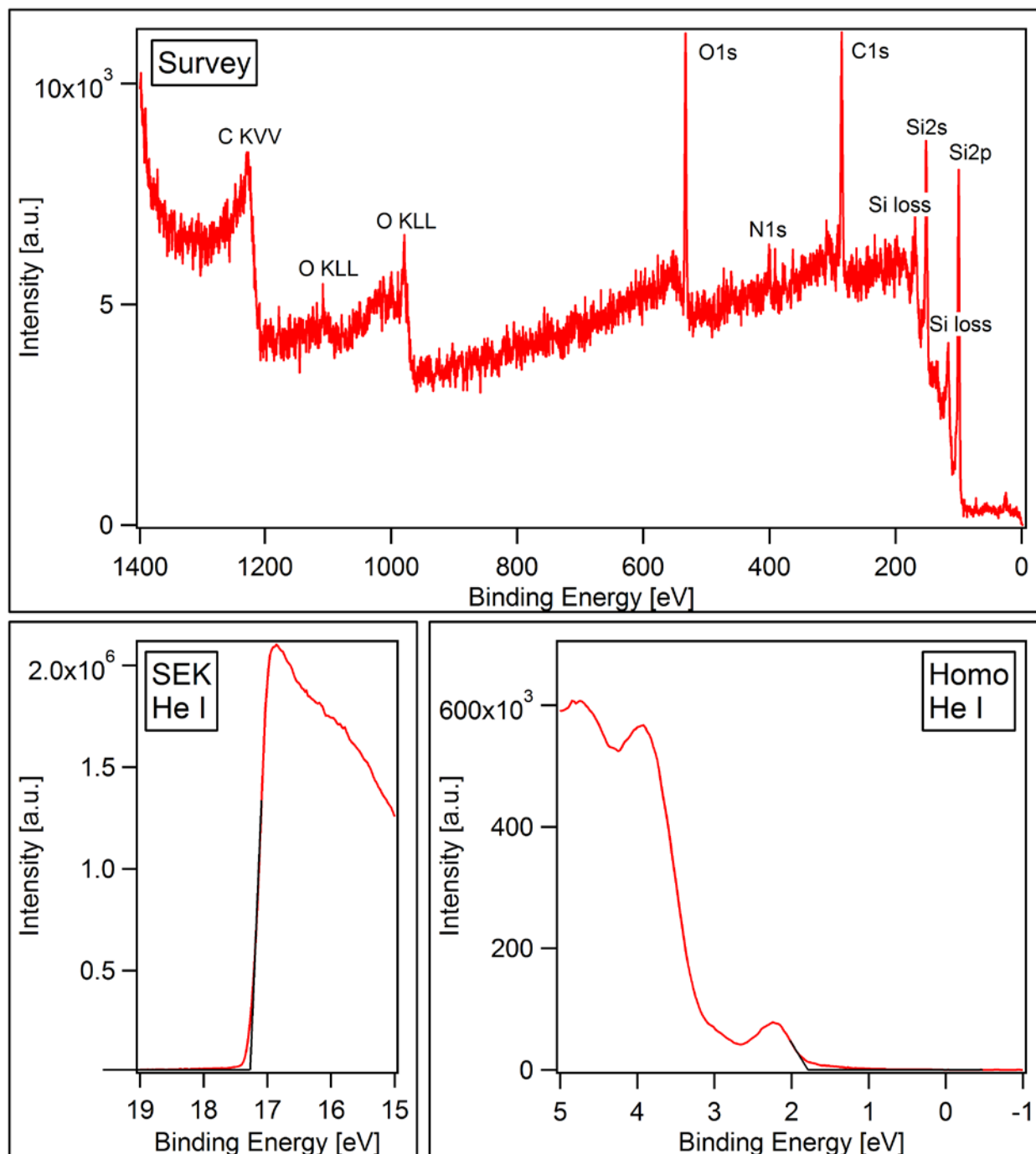
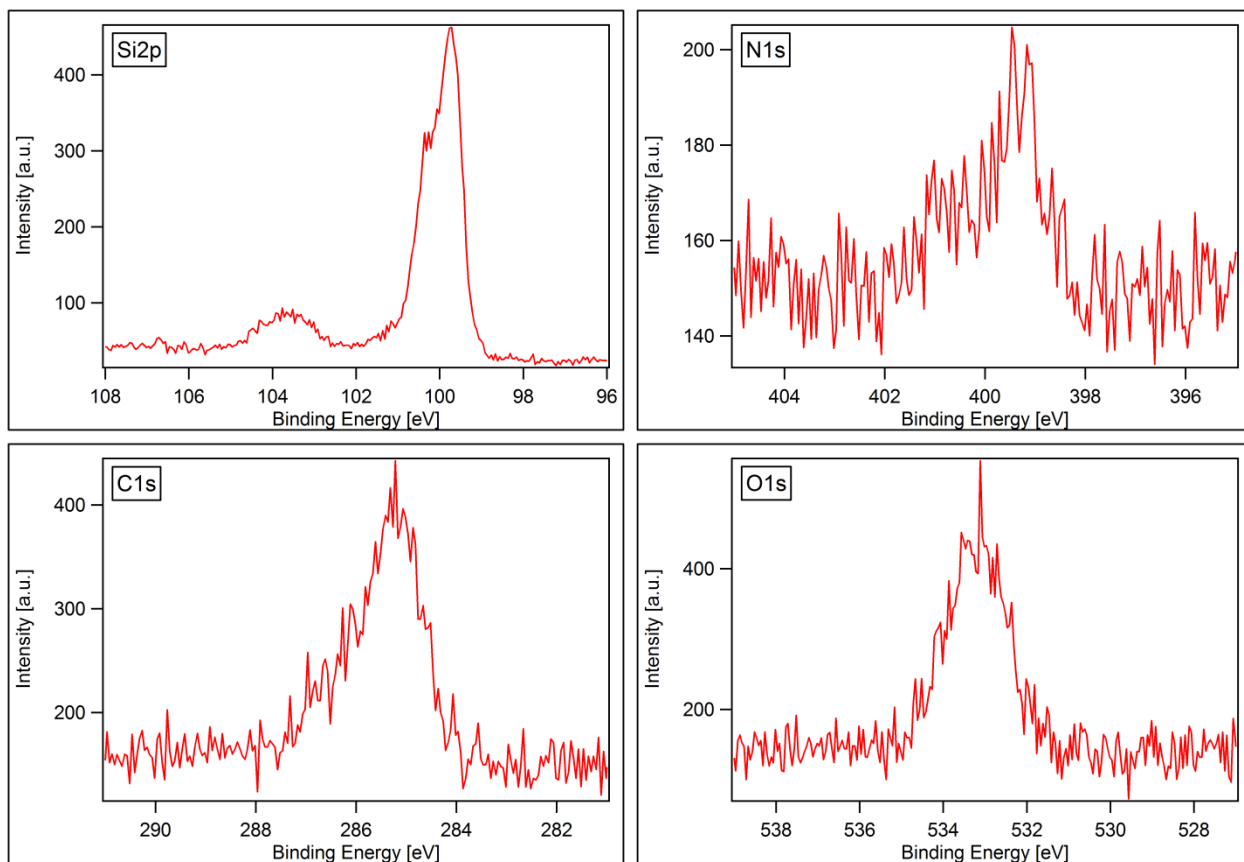


Figure S9.1.1: XPS-survey spectrum and UPS-spectra of compound 7.



**Figure S9.1.2:** Resolved atomic XPS-reflexes of compound 7.

## 9.2 1D-construct 8

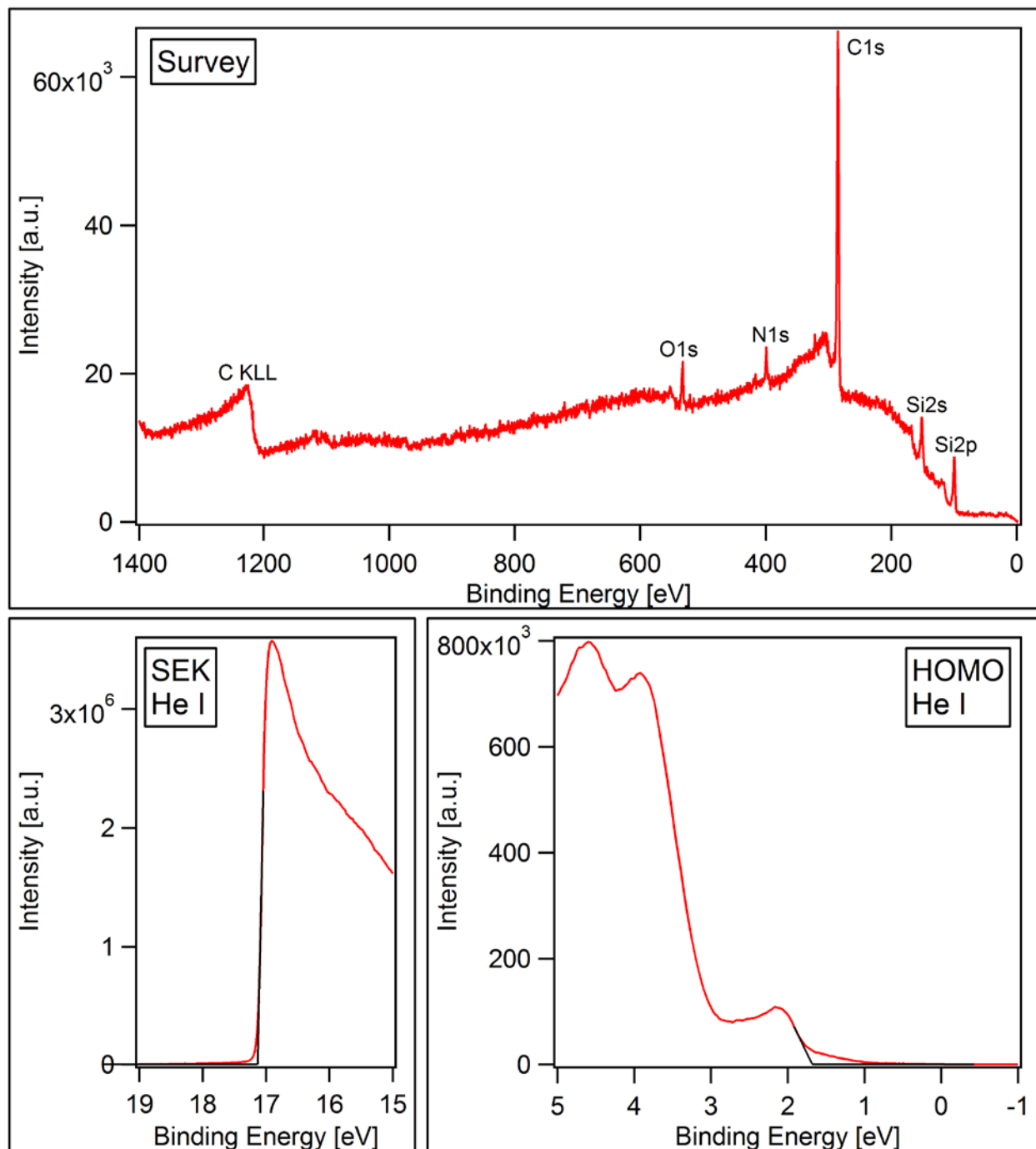
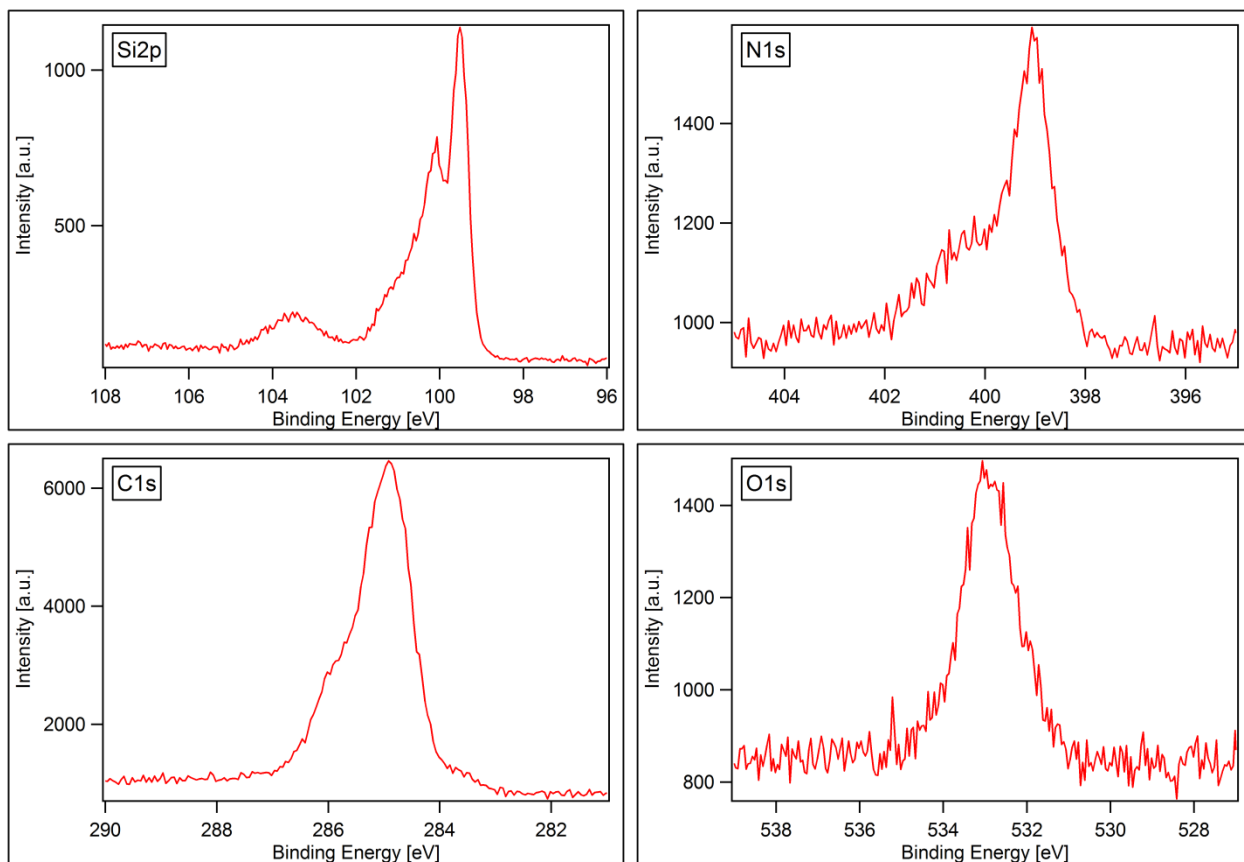


Figure S9.2.1: XPS-survey spectrum and UPS-spectra of compound 8.



**Figure S9.2.2:** Resolved atomic XPS-reflexes of compound **8**.

### 9.3 2D-construct 9

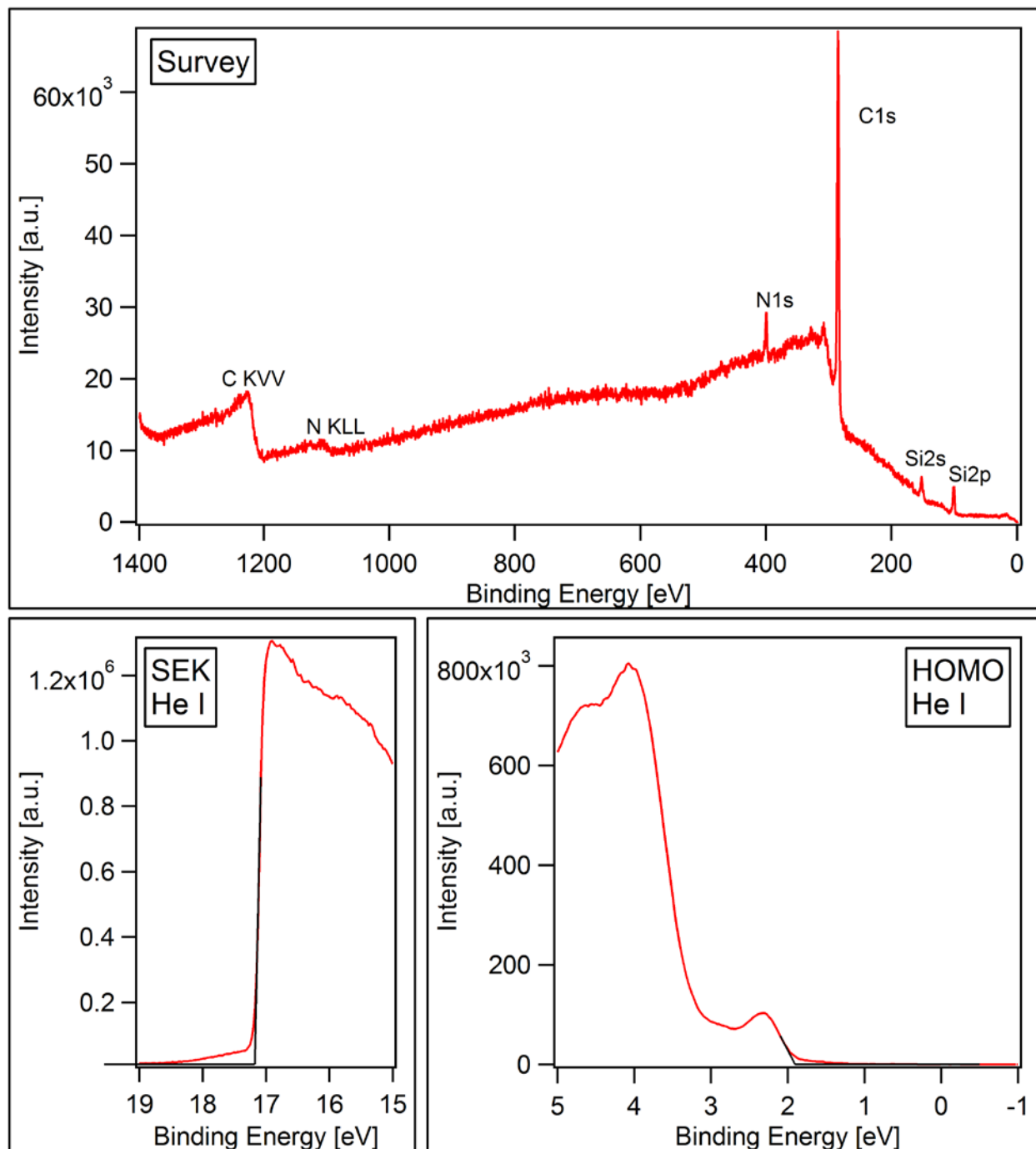
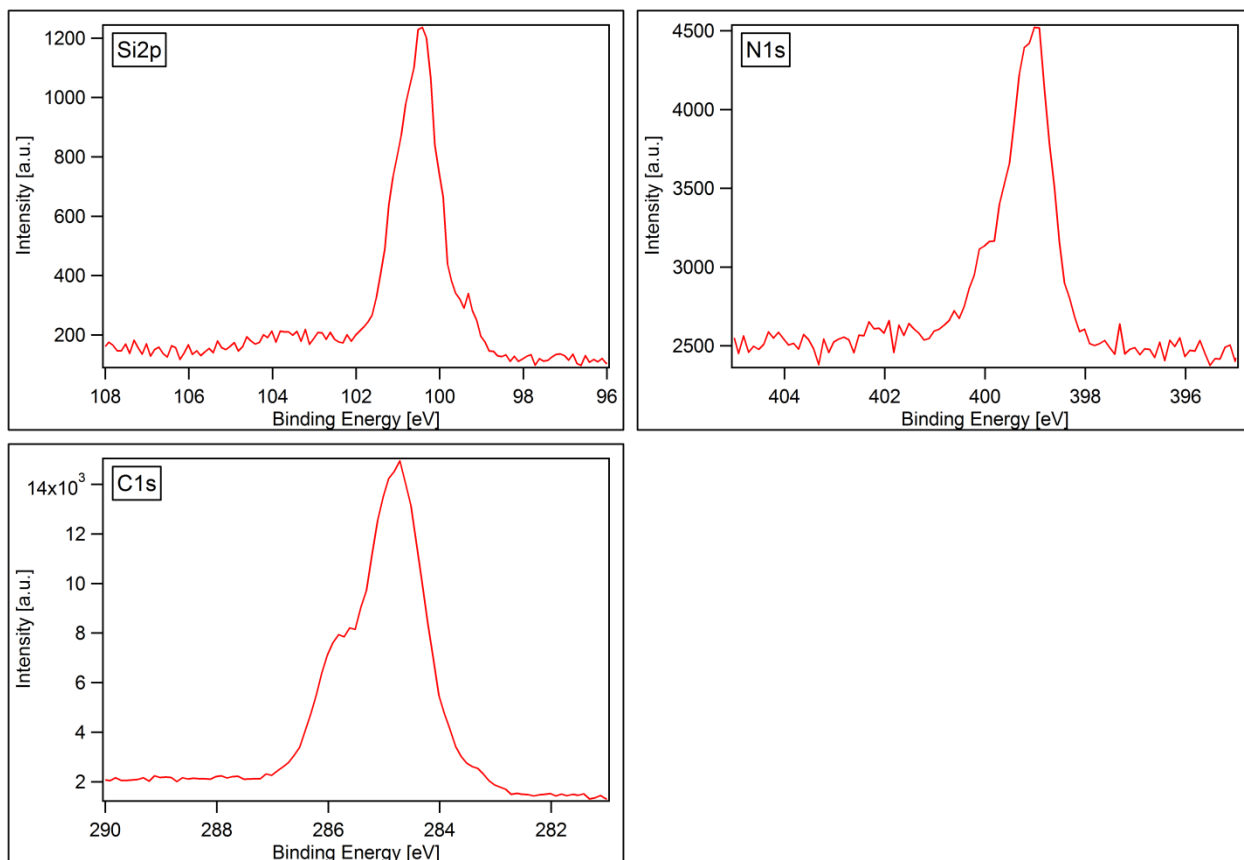


Figure S9.3.1: XPS-survey spectrum and UPS-spectra of compound 9.





**Figure S9.3.2:** Resolved atomic XPS-reflexes of compound 9.

## 9.4 2D-construct 10

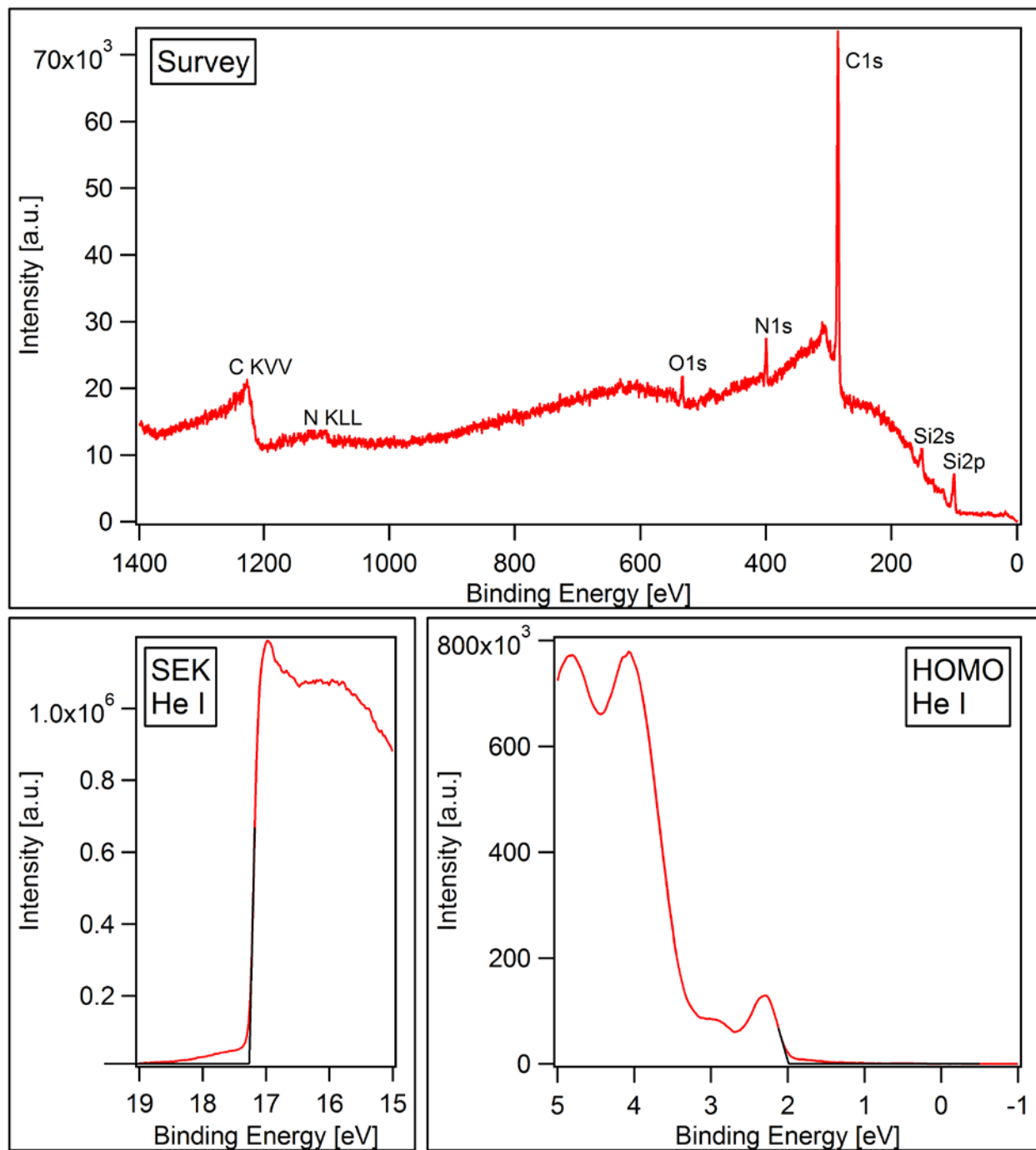
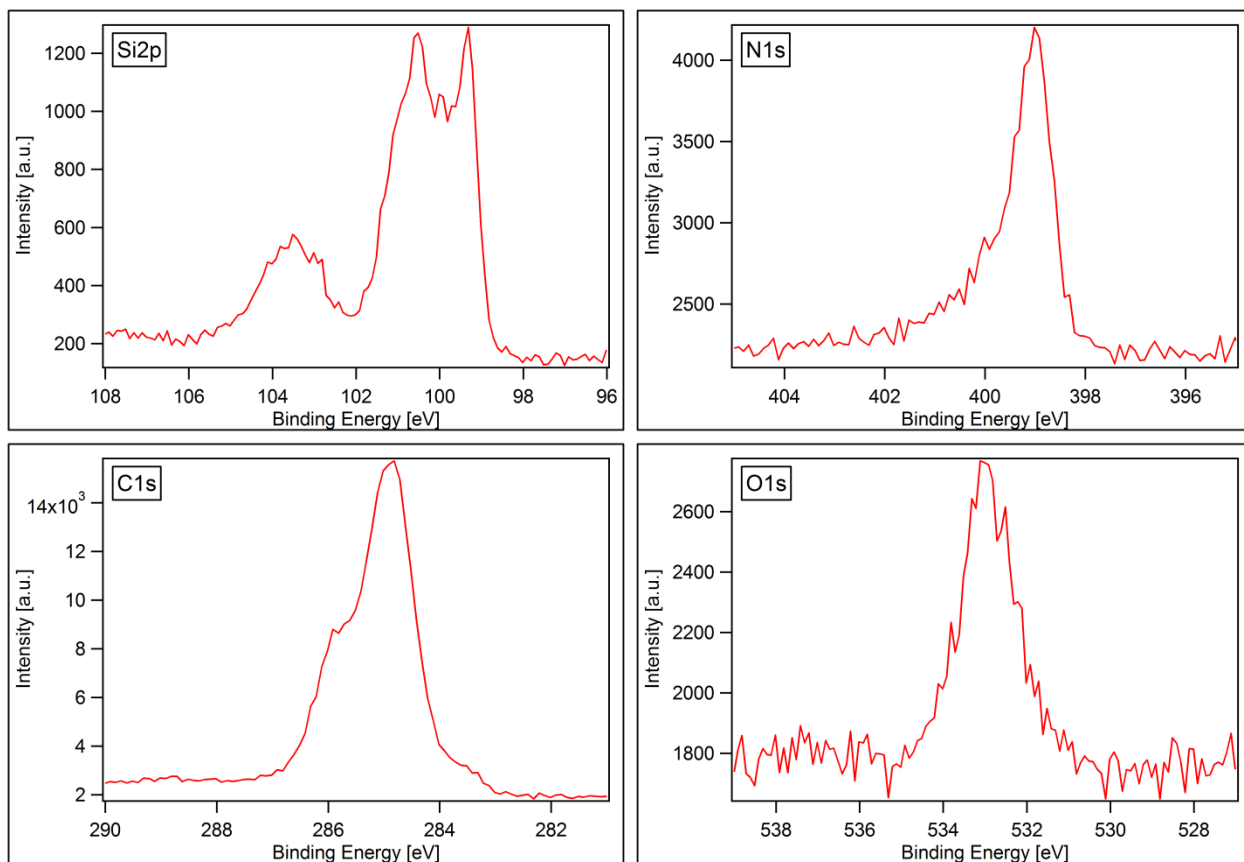


Figure S9.4.1: XPS-survey spectrum and UPS-spectra of compound 10.



**Figure S9.4.2:** Resolved atomic XPS-reflexes of compound **10**.

## 9.5 2D-construct 11

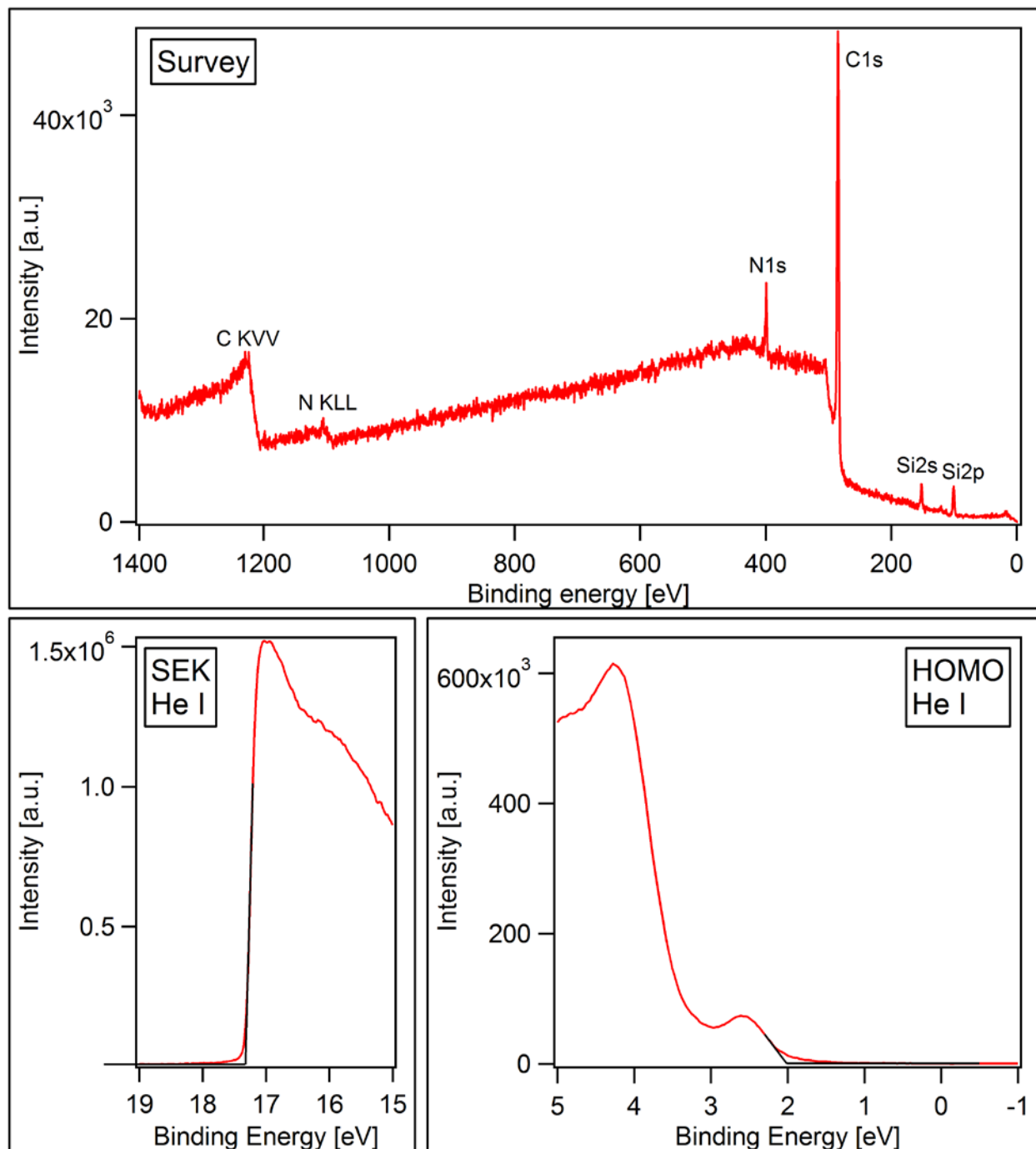
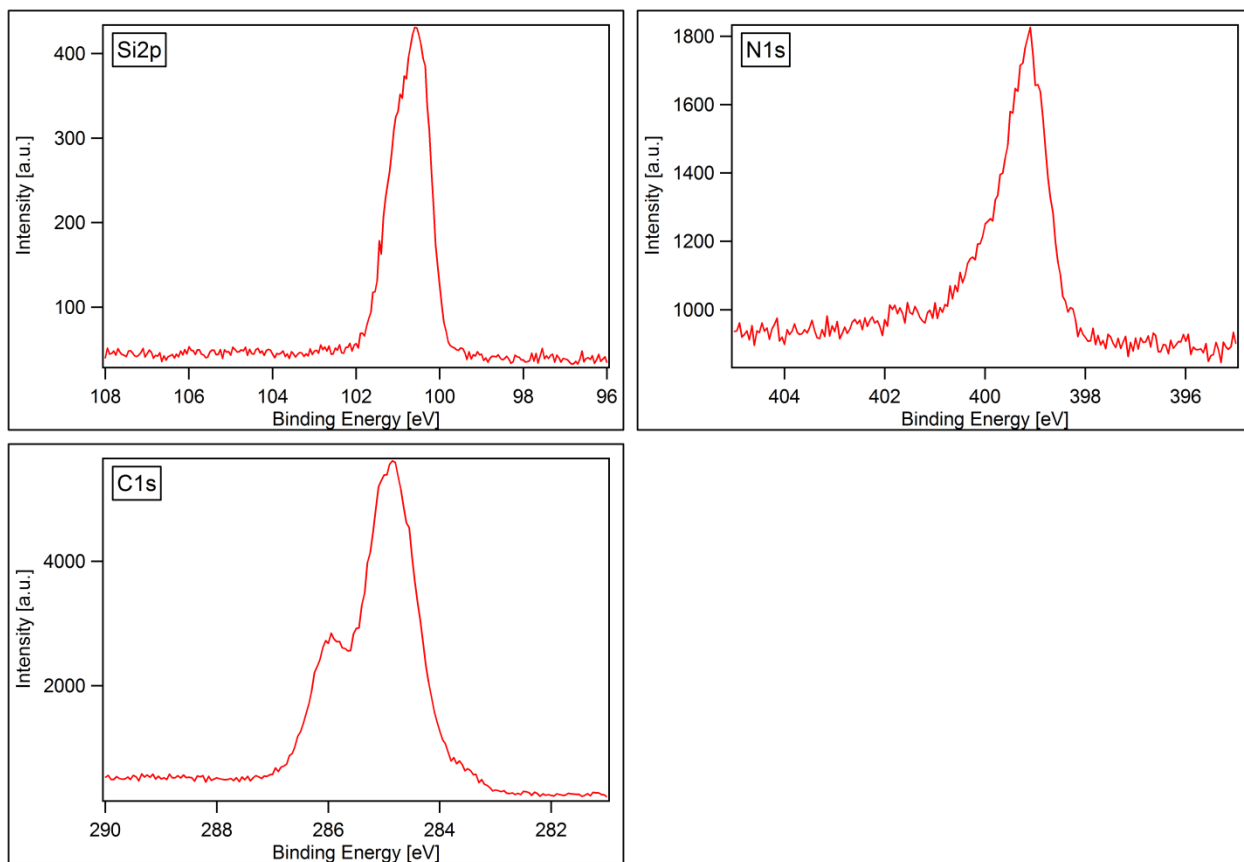


Figure S9.5.1: XPS-survey spectrum and UPS-spectra of compound 11.



**Figure S9.5.2:** Resolved atomic XPS-reflexes of compound **11**.

## 9.6 3D-construct 13

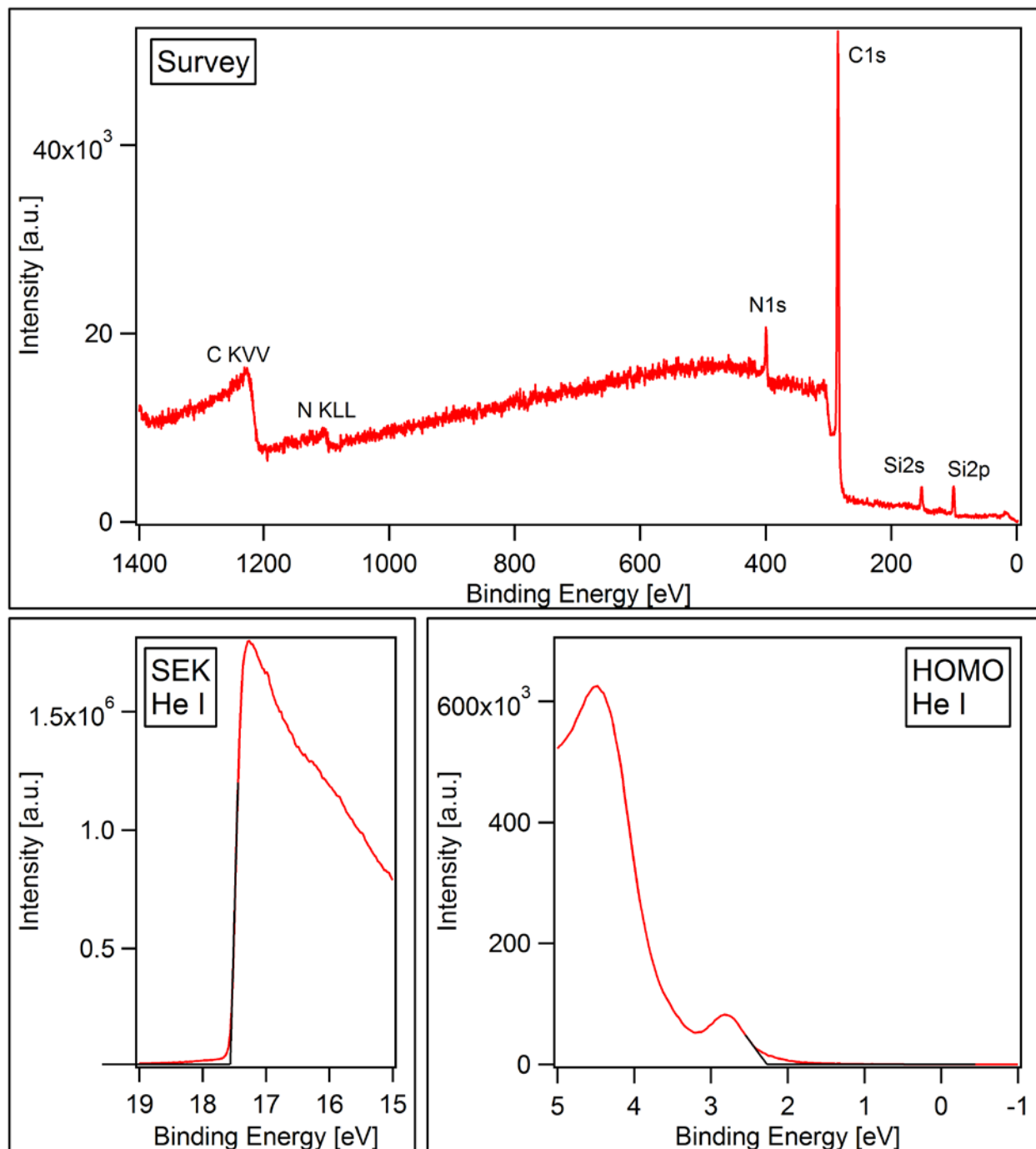


Figure S9.6.1: XPS-survey spectrum and UPS-spectra of compound 13.

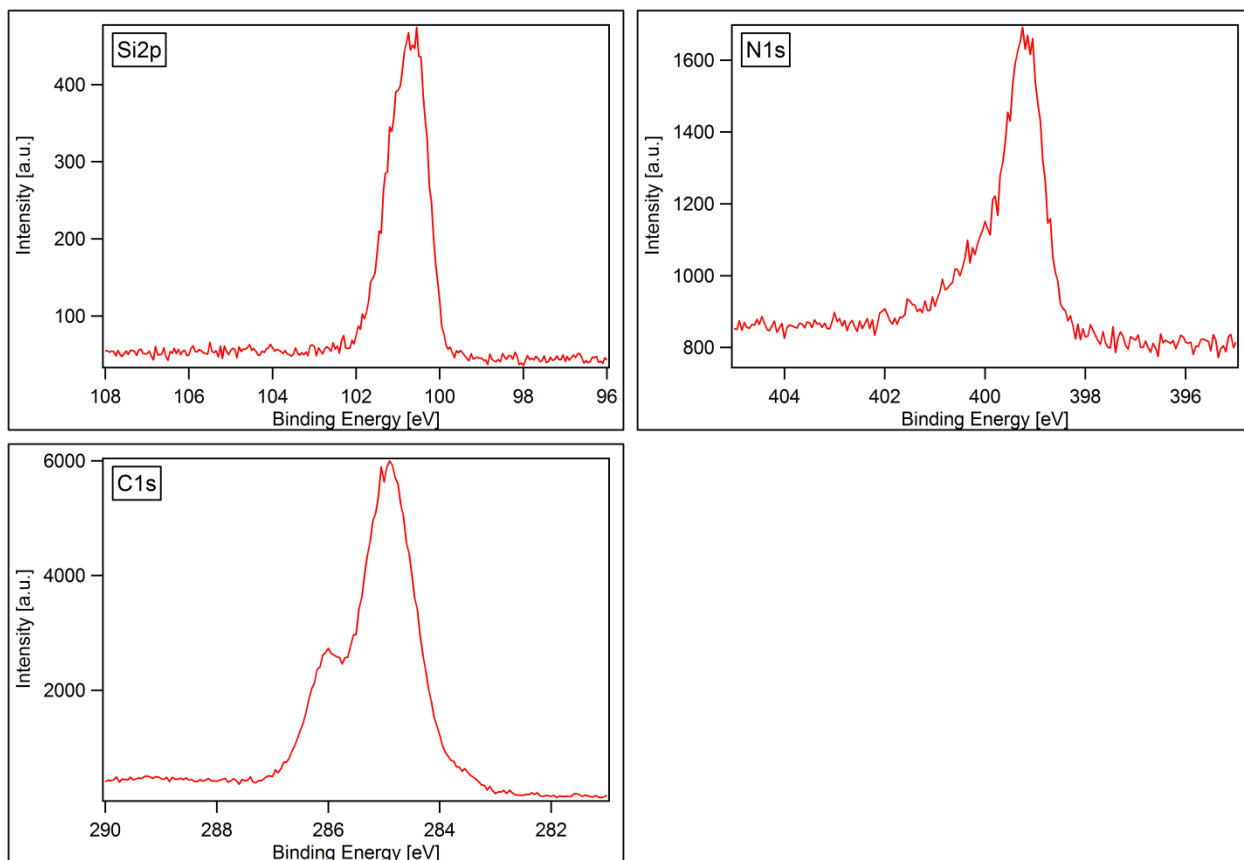


Figure S9.6.2: Resolved atomic XPS-reflexes of compound **13**.

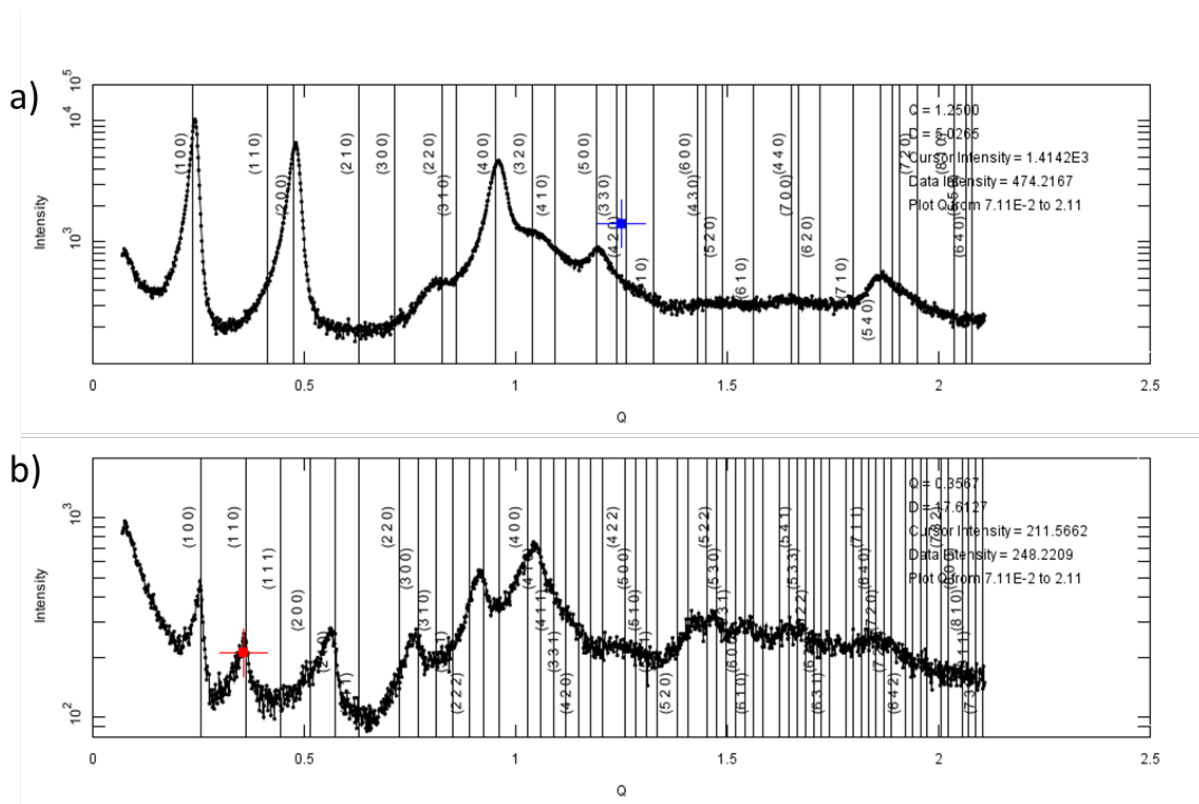
## 9.7 Determination of HOMO-energy levels (ionization potentials)

Table S9.1: Analysis of UPS-data.

dimensionality compound	1D		2D			3D
	7	8	9	10	11	13
$\Delta(\text{HOMO}_{\text{VBM}} - \text{WF}^*) \text{ He1 [eV]}$	1.79	1.68	1.90	1.99	2.01	2.27
WF*	3.95	4.09	4.04	3.96	3.89	3.66
HOMO	5.74	5.77	5.94	5.95	5.90	5.93

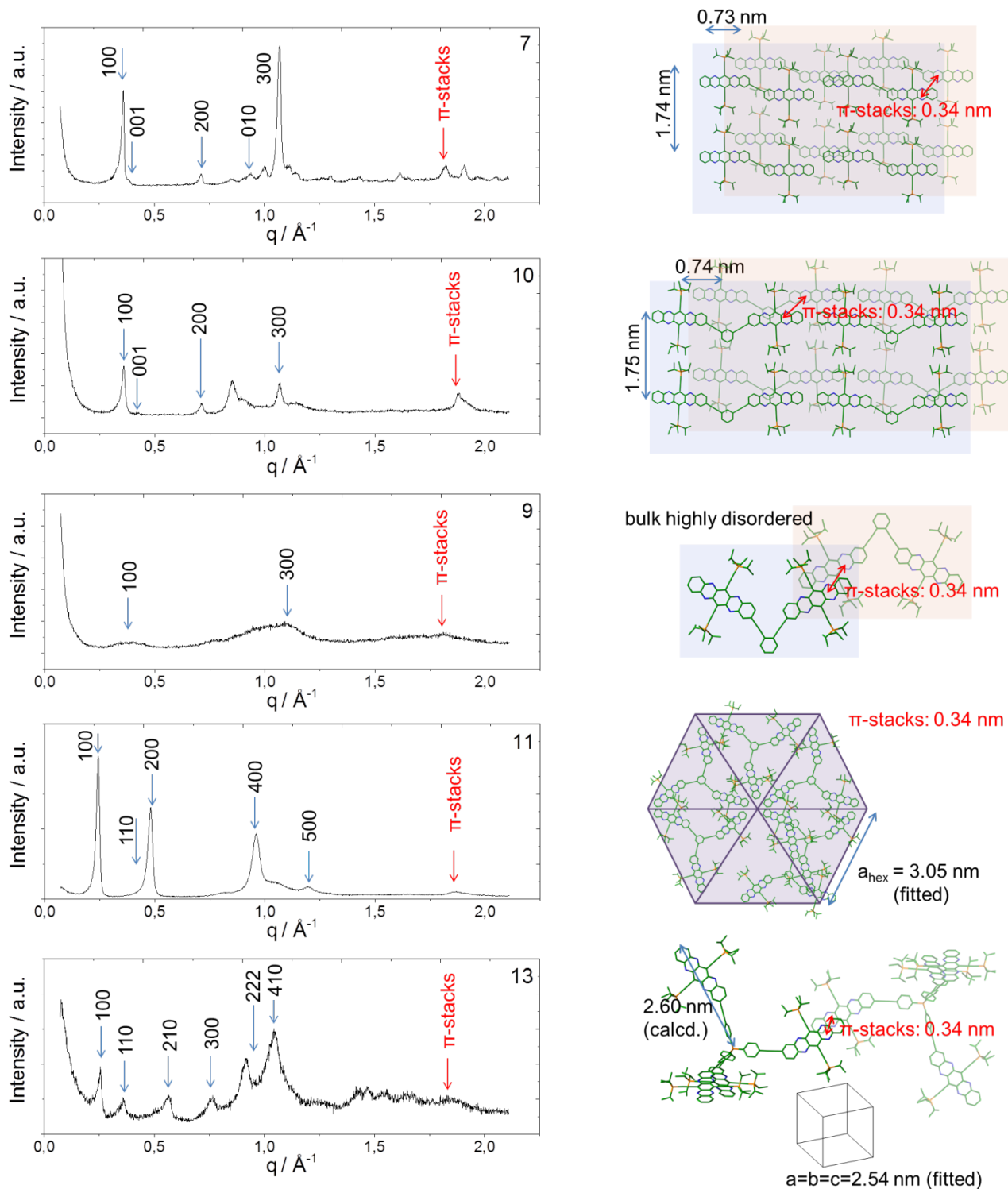
\* Workfunction

# 10 Diffractometric Characterizations



**Figure S10.1.** Theoretical adjustment to experimental 1D XRD data confirming a) hexagonal unit cell with  $a_{hex} = 3.05$  nm for compound 11 and b) simple cubic lattice with  $a=b=c=2.54$  nm created by compound 13. Theoretical simulation has been done by graphical interface for analyzing data from x-ray detectors. Datasqueeze, Version 3.0.8.





**Figure S10.2.** Diffractometric studies and corresponding packing models of constructs **7**, **9**, **10**, **11**, **13**.

There is a clear morphological trend based on the dimensionality of the linker. A small change from the line-spanning (1D) 1,4-diethynyl benzene to the plane-spanning 1,3-diethynyl benzene (2D-) as the connecting linker impacts solubility and aggregation. To gain insight into the molecular and

electronic structure of the constructs, quantum chemical calculations were carried out. These results were compared with diffractometric investigations of bulk samples. Figure 5 shows the geometry-optimized structure for each **TIPSTAP**-construct. In all structures, the linker's geometry is transferred to the overall construct. Both 1D-linkers cause the edges (C9-atoms of the azapentacenes) to span a line (1D-object), the 2D-objects to span planes and the Onsager cross **13** to span an expanded tetrahedron. The geometry-optimized structures were used for single point energy calculations (B3LYP-6311Gdp). All constructs show similar HOMO and LUMO values (-5.5 eV and -3.9 eV respectively) and accurately reproduce the gap measured in solution-UV-Vis-spectra (1.7 eV) (see SI chapter 8 for detailed information on the molecular electronic structures).

The  $\pi$ -stacking distance between individual **TIPSTAP** subunits of 0.34 nm for **7** and 0.33 nm for **10** is quite small. The lattice parameters derived from the diffraction patterns are  $a=16.4 \text{ \AA}$ ,  $b=6.7 \text{ \AA}$ ,  $c=17.5 \text{ \AA}$ ,  $\alpha= 88.5$ ,  $\beta= 91.9$ ,  $\gamma=83.6$  for **7** and for **10**

# 11 Summarized Data

**Table S11.1:** Electronic properties of TIPSTAP-constructs in solution and *in silico*. Calculations performed as described above (Energy: DFT, B3LYP 6-311Gdp)

dimensionality	Compound	reduction-potential 1/2 [V]	HOMO [eV]		LUMO [eV]		gap [eV]	
			meas. / calcd.		meas. / calcd.		meas.* / calcd.	
0 D	TIPSTAP	-0.71 / -1.17	-5.82 / -5.52		-4.09 / -3.76		1.73 / 1.76	
	5 (C <sub>2</sub> TMS)	-0.88 / -1.34	-5.62 / -5.53		-3.92 / -3.80		1.70 / 1.73	
1D	7 (ethylene)	-**	- / -5.53		- / -3.97		1.69 / 1.56	
	8 (1,4-dimer)	-**	- / -5.51		- / -3.89		1.70 / 1.62	
2D	10 (1,3-dimer)	-0.84 / -1.30	-5.66 / -5.53		-3.96 / -3.83		1.70 / 1.70	
	9 (1,2-dimer)	-0.86 / -1.49	-5.64 / -5.51		-3.94 / -3.87		1.70 / 1.64	
	11 (1,3,5-trimer)	-0.80 / -1.22	-5.70 / -5.56		-4.00 / -3.87		1.70 / 1.69	
3D	76 (Si-Onsager)	-0.79 / -1.36	-5.55 / -5.53		-4.01 / -3.86		-1.69 / -1.67	

\* determined from onset of low energy absorption maximum, see chapter 5.

\*\* due to low solubility no CV-measurements of the 1D-constructs.

**Table S11.2:** Comparison of optical properties in film and solution, for spectra see chapter 5.

dim.	compound	solution [nm] / [ eV]		film (spincoat) [nm] / [ eV]	
		$\lambda_{\max}$ / $E_{\max}$	$\lambda_{\text{onset}}$ / $E_{\text{onset}}$	$\lambda_{\max}$ / $E_{\max}$	$\lambda_{\text{onset}}$ / $E_{\text{Kante}}$
0 D	TIPSTAP	679/1.826	718/1.727	685/1.810	-*
	5 (C <sub>2</sub> TMS)	691/1.794	726/1.708	704/1.761	738 / 1.680
1D	7 (Acetylen)	699/1.774	732/1.694	717/1.729	-*
	8 (1,4-Dimer)	696/1.781	730/1.698	721/1.720	-*
2D	10 (1,3-Dimer)	694/1.787	730/1.698	709/1.749	752/1.649
	9 (1,2-Dimer)	696/1.781	731/1.696	711/1.744	752/1.649
	11 (1,3,5-Trimer)	694/ 1.787	729/1.701	709/1.749	758/1.636
3D	13 (Si-Onsager)	697/1.779	732/1.694	702/1.766	744/1.666

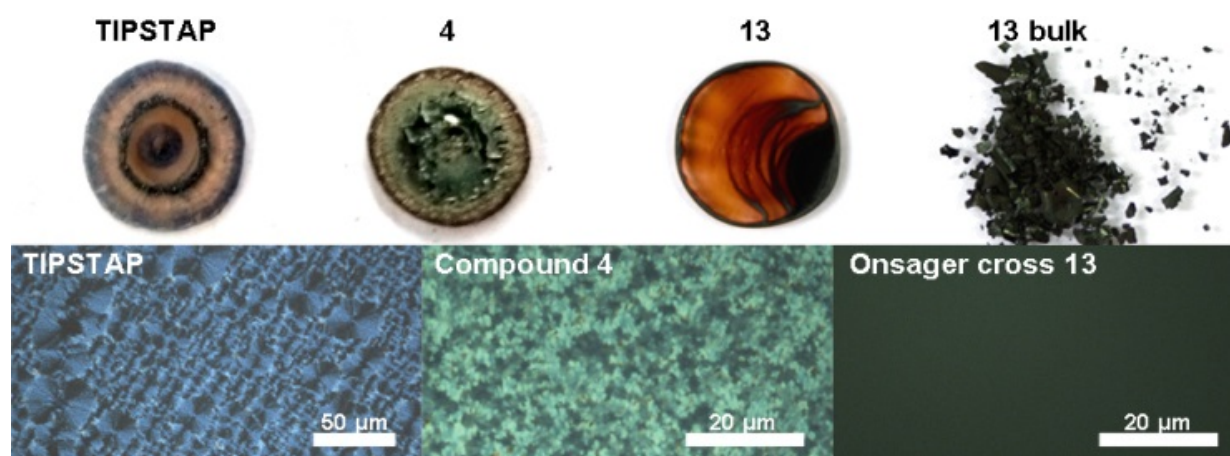
\* cannot be determined due to strong light scattering in crystalline or rough films:

**Table S11.3:** Electronic properties in thin films.

dimension	0D		1D		2D			3D	
	66	71	72	73	74	75	76	77	
HOMO	-6.08	-5.71	-5.73	-5.91	-5.86	-5.82	-5.87	-6.03	
LUMO***	-4.40	-4.07	-4.08	-4.26	-4.21	-4.18	-4.20	-4.38	
Gap	-1.68	-1.64*	-1.65*	-1.65	-1.65	-1.64	-1.67	-1.65	

\* empirically estimated from UVVis-gap in solution minus 0.05 eV

\*\* from HOMO (ionization potential) from UPS-measurements (chapter 9) by adding the optical gap determined from the onsets of the film spectra (chapter 5).



**Figure S11.** Drop cast (10 mg/mL, DCM) samples from **TIPSTAP**, phenylethynylated **4** and drop cast and bulk samples of cross **13** (top row). Film forming properties are greatly enhanced towards **13**. Polarized microscopy of spin cast films (same solutions) of these compounds (bottom row).

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