Supramolecular nanopatterns of H-shaped molecules

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Supporting Information

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1 Experimental section

1.1 Materials and equipment

All water and air sensitive manipulations were performed under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried using an MB-SPS800 solvent drying system (MBraun, Garching, Germany). Piperidine was distilled over CaH_2. Solvents used for workup of reaction mixtures and silica gel column chromatography (dichloromethane, cyclohexane, ethyl acetate, and acetone) were obtained in technical quality and distilled prior to use. All other commercially available solvents and chemicals were of reagent grade and used as received, unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker DPX 300, DPX 400 or DPX 500 (300, 400 and 500 for ^{1}H and 75, 100 and 125 MHz for ^{13}C, respectively). Chemical shifts are given in parts per million (ppm) referring to tetramethylsilane (TMS). Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS), AEI MS-5 (EI-HRMS). MALDI MS and MALDI HRMS data (recorded on a Bruker Daltonics Apex IV FT-ICR) are given for the high-molecular weight materials (matrix material: dithranol or DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile), no salts added). *m/z* peaks smaller than 10 % (compared to the basis peak) are not reported. Thin layer chromatography was performed on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV_{254} 0.25 mm coating with fluorescence indicator). Silica gel 60 M (Macherey-Nagel, 0.040 – 0.063 mm) was used as the stationary phase for column chromatography. A Shimadzu Recycling GPC System, equipped with an LC-20 AD pump, an SPD-20 A UV detector, and a set of three preparative columns (10^2-10^5 Å, 3 mm, 5 mm, 10 mm, 20 x 300 mm, SDV linear S) from PSS (Mainz, Germany) was used for product separation and purification.

1.2 STM investigations

Scanning tunneling microscopy (STM) was performed under ambient conditions (room temperature) at the solution/solid interface of 1,2,4-trichlorobenzene (TCB) and highly oriented pyrolytic graphite (HOPG). Typically, about 0.5 µL of a 10^{-4}–10^{-7} M solution of the compound of interest in TCB was dropped onto to a piece of freshly cleaved HOPG at elevated temperature (Figure 3–5 (Main Text) and Figures S3–S8: 80 °C, Figure 6 and Figures S9–S10: 120 °C), kept at the temperature for a few seconds (Figures 3–5 (Main Text) and Figures S3–S8): 20 s, Figure 6 (Main Text) and Figure S9–S10: 10 s), and allowed to cool to r.t. prior to

imaging. All STM measurements were performed *in situ* (with the tip immersed into the solution) and typically completed within 30 min after sample preparation. In this work, bias voltages between –0.6 and –1.2 V and tunneling currents in the range of 7–21 pA were applied to image the molecular adlayers.

The experimental setup consists of an Agilent 5500 scanning probe microscope that is placed on a Halcyonics microscopy workstation with an active damping unit, and it is acoustically isolated with a home-built noise damping box. Scissors cut Pt/Ir (80/20) tips were used and further modified after approach by short bias voltage pulses. HOPG was obtained from Mikromasch in ZYB quality and freshly cleaved prior to each experiment. All STM images (unless otherwise noted) were *in situ* calibrated by subsequent immediate acquisition of an additional image at reduced bias voltage, therefore the atomic lattice of the HOPG surface is observed which is used as a calibration grid. Data processing, also for image calibration, was performed using the SPIP 5 (Image Metrology) software package. (Supra-) molecular modelling was performed using Spartan `08 and Spartan `10 (Wavefunction, Inc.).

2 Additional molecular models

2.1 Equilibrium geometry of the 1*H*-benzimidazole building block

The geometry of the H-shaped molecules **1**–**4** relies on 2,4,7-trisubstituted 1*H*-benzimidazole building blocks that can be viewed as T-shaped joint units. 4,7-diethynyl-2-phenylene-1*H*-benzimidazole (Figure S1a) is discussed as a model compound, and its gas phase equilibrium geometry (calculated at the 6-31G*/B3LYP level of density functional theory) is shown in Figure S1b,c (space-filling model) and Figure S1d,e (ball-stick model). The phenyl substituent at the 2 position of the heterocyclus is oriented coplanar to the latter. The axis c_3, defined as the connection line between the C1 and C4 atoms of the phenyl substituent, is orthogonal ($\gamma(c_1,c_3)$ = 90°) to the axis c_1 that is defined by the ethynyl carbon atoms. Both ethynyl units form a straight line ($\gamma(c_1,c_2)$ = 180°). Consequently, *1*H-benzimidazole can be viewed as a T-shaped building block in **1**–**4**.

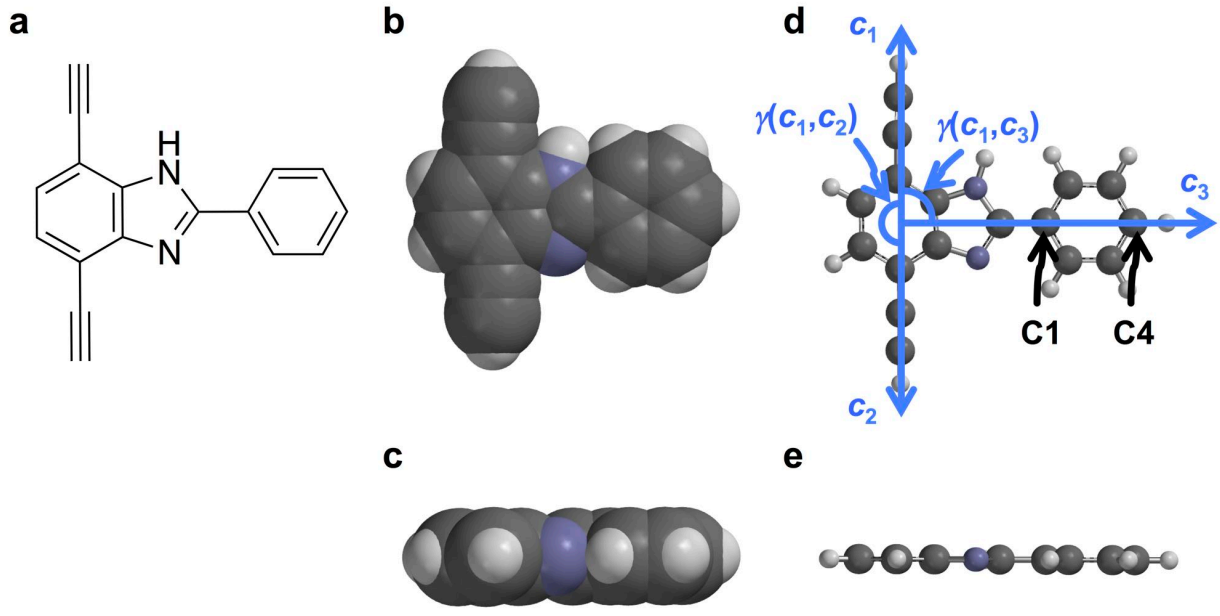


Figure S1. 4,7-Diethynyl-2-phenylene-1*H*-benzimidazole as model system for T-shaped building blocks in **1**–**4**: (a) Chemical structure and (b)–(e) equilibrium geometry (DFT, 6-31G*, B3LYP); in particular: (b)–(c) space-filling models in (b) top view and (c) side view; (d)–(e) ball-stick models in (d) top view ($\gamma(c_1,c_2)$ = 180°; $\gamma(c_1,c_3)$ = 90°) and (e) side view.

2.2 Additional molecular models of 1

In the molecular model of **1** shown in Fig 2 (Main Text), the equilibrium geometry of the H-shaped backbone with subsequently added all-*trans* configured alkoxy side chains (oriented perpendicular to the backbone) and (3-cyanopropyl)diisopropylsilyl (CPDIPS) groups[1,2] is shown, and a reprint of this structure is shown in Figure S2a. In addition, a cutout of the supramolecular model from Fig 3b (Main Text) is shown in Figure S2b. An alternative conformer (Figure S2c), leading to a closer alignment of the nitrile functions of the CPDIPS end groups, is shown. Nitrile functions oriented in antiparallel fashion and interacting *via* dipole-dipole interactions should stabilize the network formed. However, throughout all STM images of **1** (Figure S2a, Main Text, and additional STM images, Figure S5) the CPDIPS groups are not resolved with a resolution allowing to clearly distinguish a possible intra- *vs.* intermolecular interaction. In addition to the conformer shown in Figure S2a, a model with the nitrile groups oriented in antiparallel direction to interact intramolecularly is shown (Figure S32).

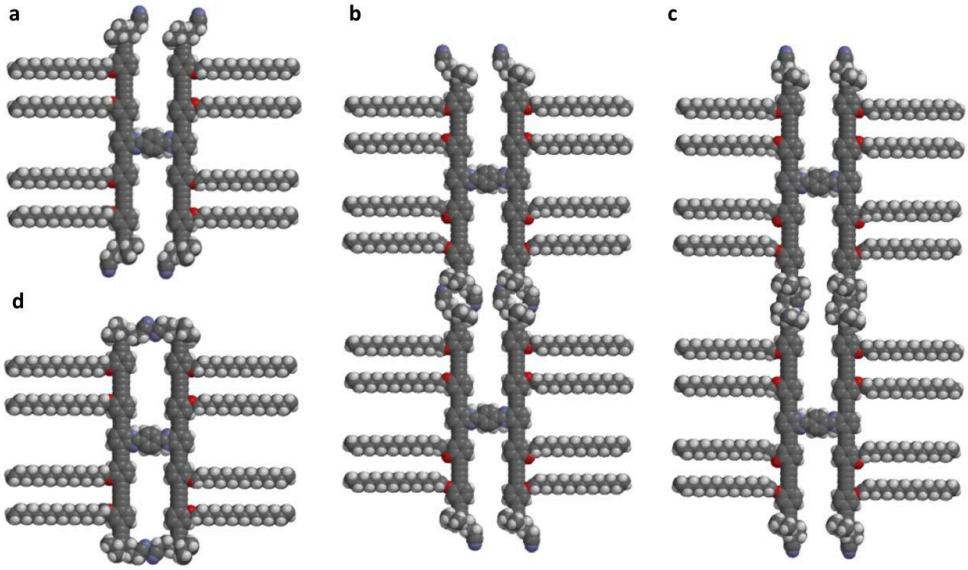


Figure S2. (a) Copy of the molecular model of **1** (as shown in Fig 2, Main Text); (b) cutout of the supramolecular model from Fig 3b (Main Text); (c) alternative model showing a different conformer of 1, in which the CPDIPDS end groups are more closely packed and aligned in parallel; (d) molecular model of **1** with both nitrile substituents of each pair of CPDIPS groups oriented in antiparallel direction.

2.3 Equilibrium geometries of 1–4

Equilibrium geometries of the phenylene-ethynylene-butadiynylene backbones of **1–4** with subsequently attached alkoxy side chains and end groups are shown in Figure S3. The sizes of the molecules are given as widths, w_n, lengths of side chains, l_n, distances of N atoms in CPDIPS groups $d_{N–N,n}$, or H atoms in biphenyl groups, $d_{H–H}$, and tile sizes, w_n, for n = **1–4**.
(Note: The concept of tiling is discussed on p. 20.)

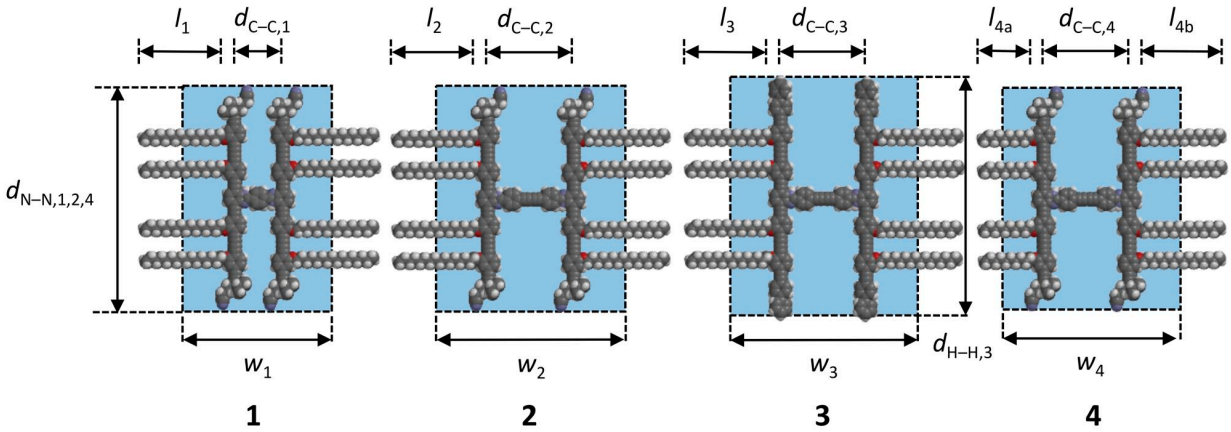


Figure S3. H-shaped molecules **1–4** with assignment of equilibrium rod-rod (center-to-center) distances, $d_{C–C,n}$, alkoxy chain lengths, l_n, end group distances, $d_{N–N,n}$ and $d_{H–H,3}$, and tile widths w_n, n = 1–4 (see Table 1). Blue rectangles illustrate the "tiles" of **1–4** (according to the concept of tiling described on p. 20).

compound		1	2	3	4	
$d_{C–C,n}$ / nm	rod-rod distance	1.2	2.2	2.2	2.2	
l_n / nm	alkoxy side chain length	2.1	2.1	2.1	1.3	2.1
$d_{N–N,n}$ or $d_{H–H,3}$ / nm	end group distance (≈ length of „tile“)	5.4	5.4	6.0	5.4	
w_n / nm	width of „tile“	3.8	4.8	4.8	4.5	

Table S1. $d_{C–C,n}$, l_n, $d_{N–N,n}$, $d_{H–H,3}$, and w_n (n = 1–4) of **1–4**. For assignments see Figure S3.

3 Additional STM images

3.1 STM images of 1

An enlarged reprint of Figure 3 (Main Text) is shown in Figure S4.

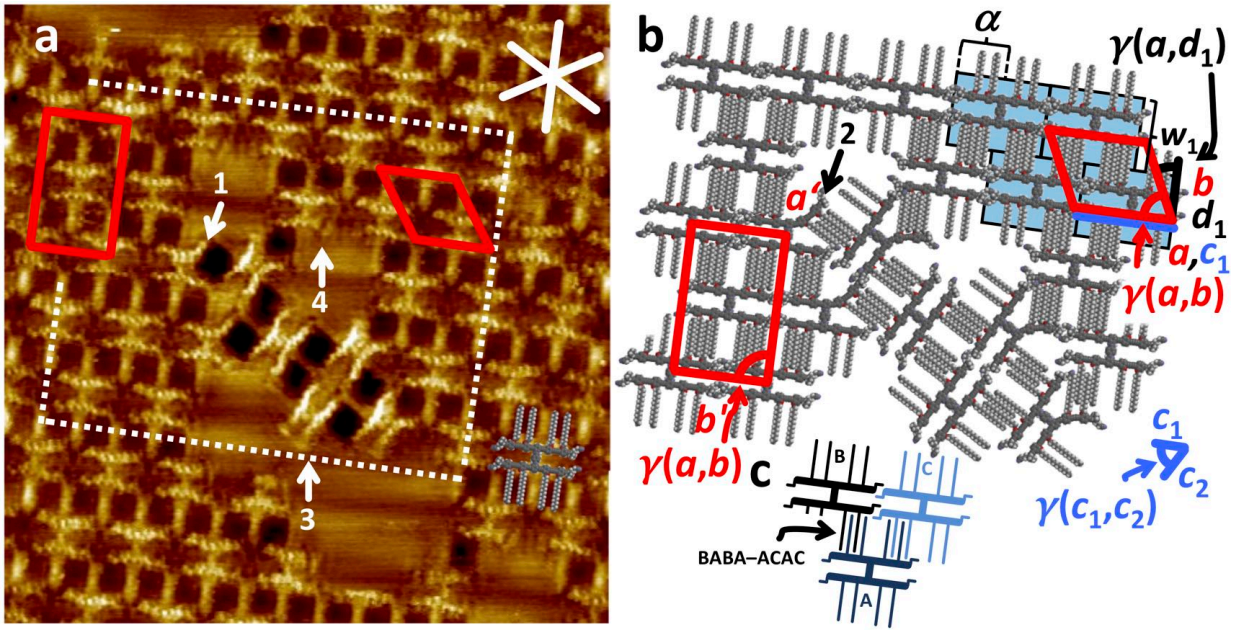


Figure S4. Reprint of Fig 3 (Main Text). **(**a) STM image, (b) supramolecular model, and (c) schematic model of **1** at the TCB/HOPG interface. Image and packing parameters: 40.0 × 40.0 nm^2, V_S = –1.2 V, I_t = 13 pA, c = 10^{-7} M; a = (5.1 ± 0.2) nm, b = 4.8 ± 0.2) nm, $\gamma(a,b)$ = (60 ± 2)°, $\gamma(a,c)$ = (0 ± 2)°, $\gamma(a,d_1)$ = (90 ± 2)°, $\gamma(c_1,c_2)$ = 60°. a' = (4.8 ± 0.2) nm, b' = 8.0 ± 0.4) nm, $\gamma(a',b')$ = (90 ± 2)°. The model in (b) shows a transcript of the marked region of (a). Red, blue, and white (black) lines indicate the unit cells, backbone (rod) directions, and HOPG main axis directions, respectively. Blue rectangles indicate the tiling indexed to **1** (slide vector a = 0.5).

Additional STM images of **1** on HOPG are shown in Figure S5. At a concentration of 10^{-7} M, a submonolayer coverage (coverage degree: $\theta = 0.5$) is observed (Figure S5). Depending on the actual PtIr tip, the PEB backbones (Figure S4b) or the CPDIPS endgroups (Figure S4c) appear bright. Figure S5c shows that the terminal CPDIPS groups (i.e., bright dots) point towards each other in the supramolecular assembly. Figure 5d shows partly imaged molecules at the domain edge (upper parts of image), most probably due to desorption during image acquisition (slow scan direction: bottom to top).

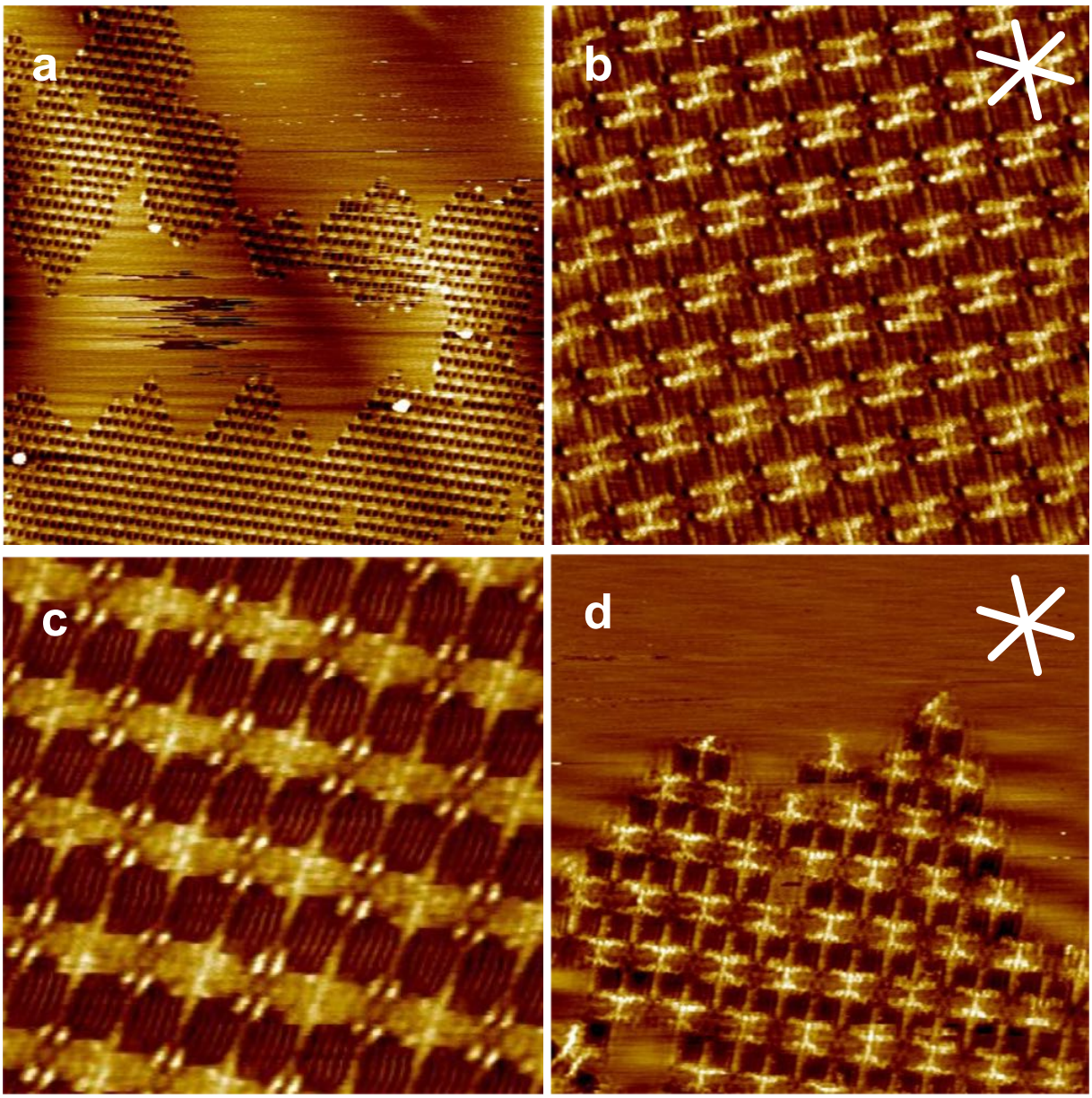


Figure S5. Additional STM images of **1**. (a) Overview STM image (190 × 190 nm^2 (internal scanner calibration), V_S = –1.0 V, I_t = 10 pA, c = 10^{-7} M, (b)–(d) High-resolution STM images (b: 36.6 × 36.6 nm^2, V_S = –1.4 V, I_t = 9 pA, c = 10^{-6} M; c: 23 × 23 nm^2 (internal scanner calibration), V_S = –1.0 V, I_t = 8 pA, c = 10^{-7} M; d: 42.9 × 42.9 nm^2, V_S = –1.2 V, I_t = 20 pA).

3.2 STM images of 2

An enlarged reprint of Figure 4 (Main Text) is shown in Figure S6.

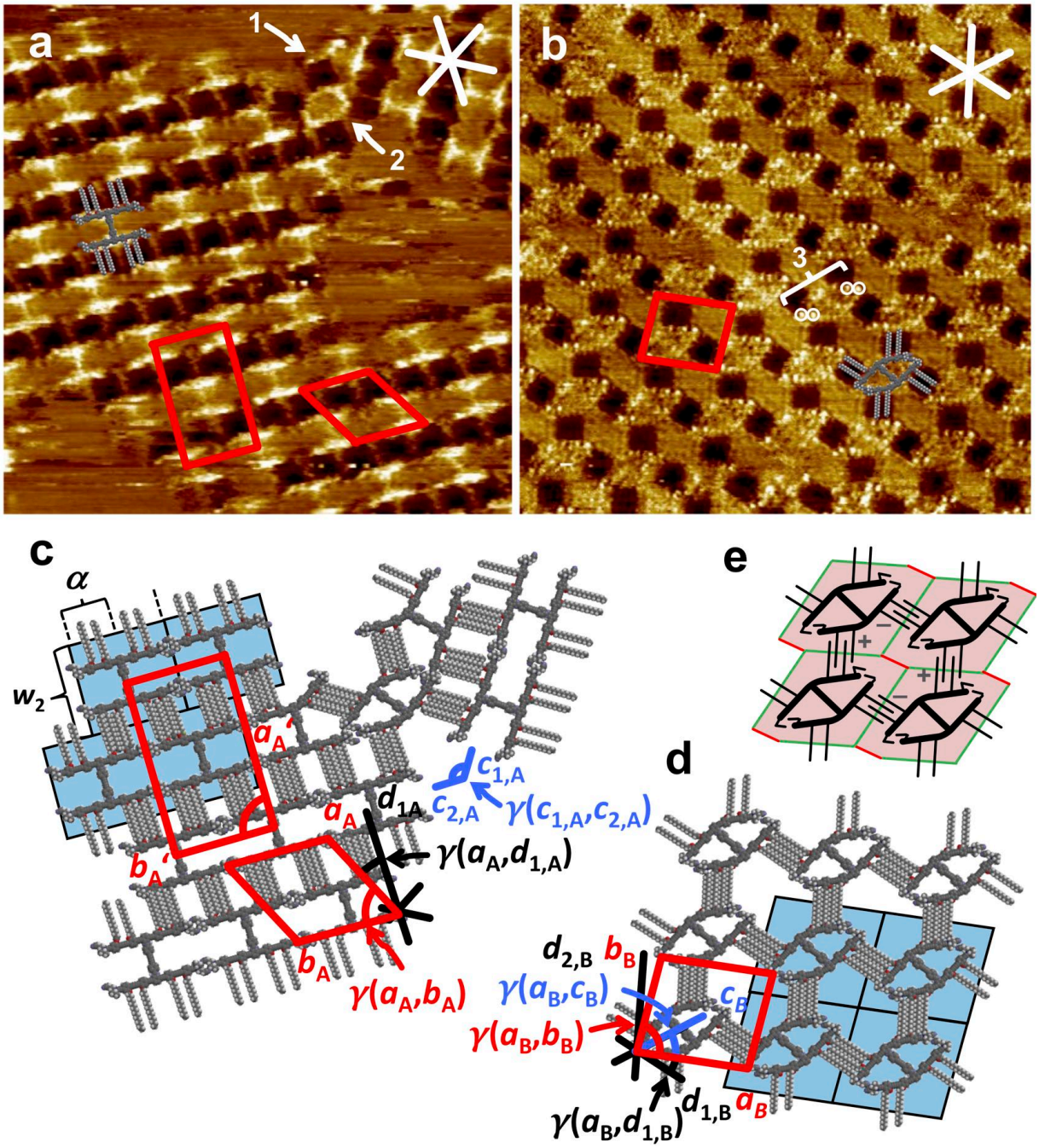


Figure S6. Reprint of Fig 4 (Main Text). (a)–(b) STM images, (c)–(d) supramolecular models, and (e) schematic model of (a), (c) polymorph A and (b), (d)–(e) polymorph B of **2** at the TCB/HOPG interface. Image and packing parameters: a,c: 35.3 × 35.3 nm^2, V_S = –1.0 V, I_t = 20 pA, c = 10^{-6} M; a_A = (5.3 ± 0.2) nm, b_A = (5.2 ± 0.2) nm, $\gamma(a_A,b_A)$ = (60 ± 2)°, $\gamma(b_A,d_A)$ = (87 ± 2)° (and a_A' = (9.6 ± 0.3 nm), b_A' = (5.0 ± 0.2) nm, $\gamma(a_A',b_A')$ = 90°); b,d: 39.3 × 39.3 nm^2, V_S = –0.6 V, I_t = 7 pA, c = 10^{-7} M; a_B = (6.0 ± 0.2 nm), b_B = (5.2 ± 0.2) nm, $\gamma(a_B,b_B)$ = (84 ± 2)°, $\gamma(a_B,c_B)$ = (36 ± 2)°, $\gamma(a_B,d_{1,B})$ = (24 ± 2)°. Red and white (black) lines indicate unit cells and HOPG main axis directions, respectively. Blue arrows represent backbone orientations (in (b), (d) defined as perpendicular bisectors through the CPDIPS units). Blue (rosé) tetragons (hexagons) in (c)–(e) indicate tilings indexed to **2**.

Overview STM images of self-assembled monolayers of **2** are shown in Figure S7. As mentioned in the Main Text, a concentration dependent polymorphism was observed. At high concentrations (c = 10^{-6} M) the molecules predominantly form polymorph A („brick-like" packing, non-edge-to-edge tiling) even though a coverage degree θ of only 67 % is observed (see Figure S7a). At lower concentrations (c = 10^{-7} M) under otherwise identical conditions, polymorph 2 (collapsed backbones) is found (here: STM image in Figure S7b with coverage degree of θ = 84 %).

Box 1 in Figure S7b indicates 6 molecules of **2** close to/at a domain edge of polymorph B. While each molecule in polymorph B (within the domain) adopts a coordination number (CN) of 4 (with respect to the alkoxy side chain interdigitation with adjacent molecules), arrow 1 indicates a molecule that adopts CN = 3. In particular, the phenylene-ethynylene-butadiynylene (PEB) unit the alkoxy side chains of which do not interdigitate intermolecularly appear blurred, which is attributed to an oscillatory motion (in the direction indicated by arrow 2) faster than the timescale of measurement.

Box 2 in Figure S7b frames two molecules that pack in a different fashion as compared to the other molecules in polymorph B of **2**. Each of the two molecules (considered here) interacts with 3 neighbouring molecules. While the two PEBs marked by arrows 3 and 4 interact with two adjacent molecules along two different HOPG main axis directions (differing in 60° angle), the two PEBs marked by arrows 5 and 6 interact with two PEBs of (only) one neighbouring PEB. This packing motif has not been observed as a general interaction motive in a 2D periodic pattern of **2** (nor of **1**), but is only found as packing defect.

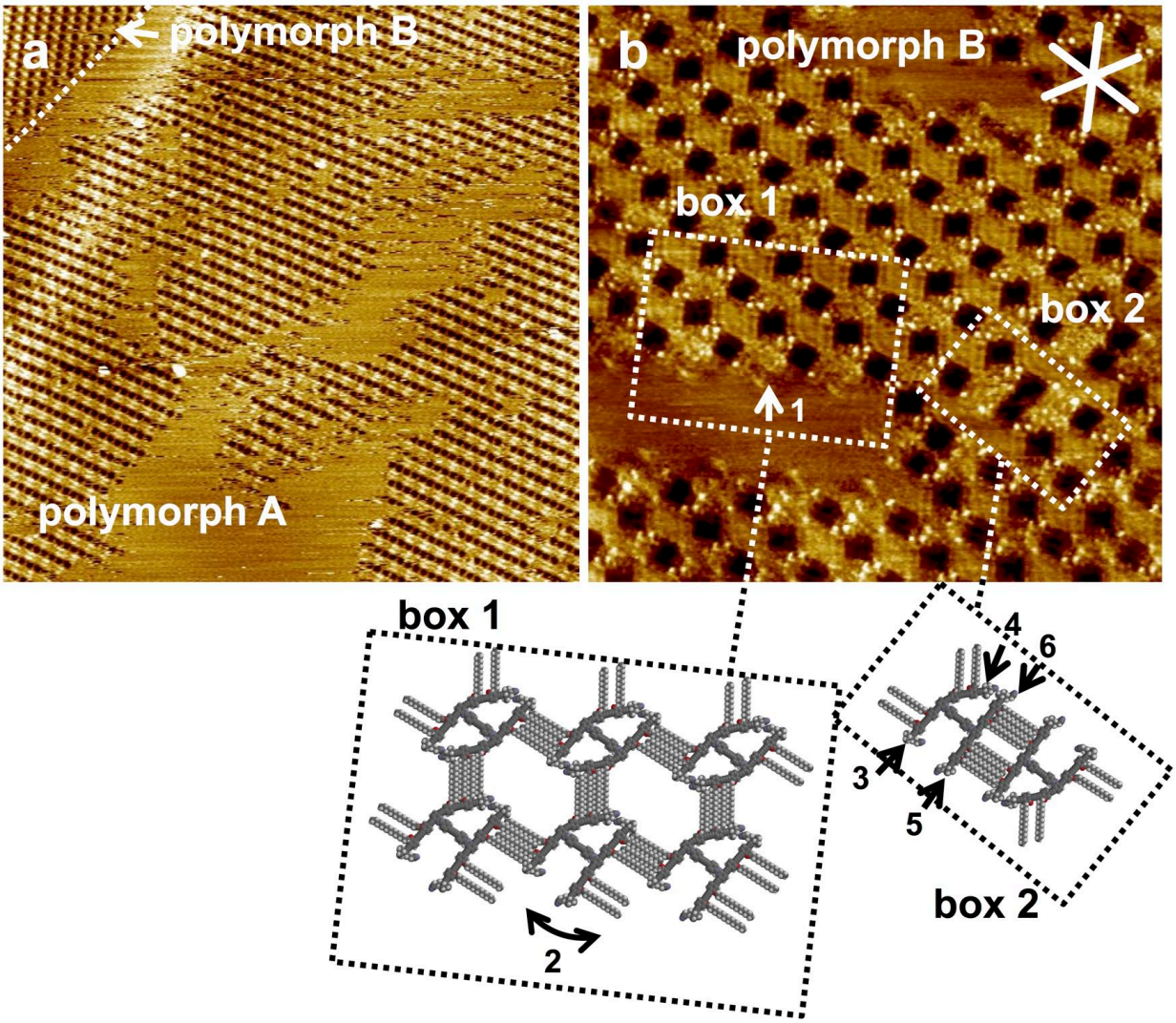


Figure S7. STM images of self-assembled monolayers of **2** at the TCB/HOPG interface. (a) Polymorph 1: 190×190 nm^2 (internal scanner calibration), V_S = –1.0 V, I_t = 7 pA, c = 10^{-6} M, θ = 67 %; (b) polymorph 2: 43.2×43.2 nm^2, V_S = –0.9 V, I_t = 14 pA, c = 10^{-7} M, θ = 84 %.

3.3 STM images of 3

An enlarged reprint of Figure 5 (Main Text) is shown in Figure S8.

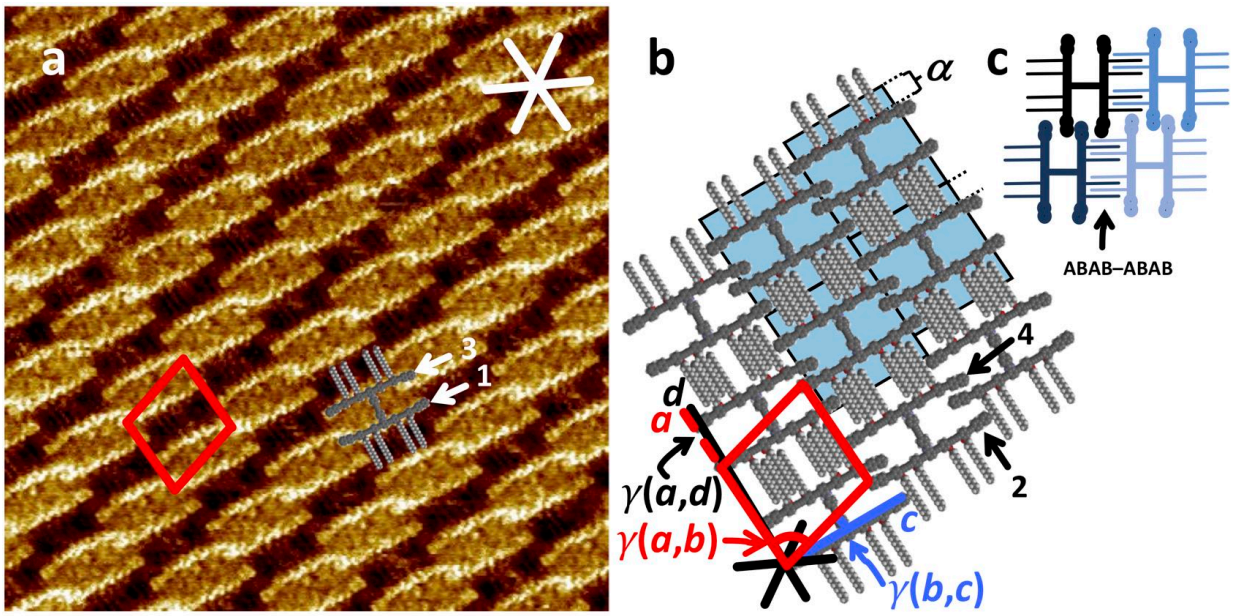


Figure S8. Reprint of Figure 5 (Main Text). (a) STM image, (b) supramolecular model, and (c) schematic model of **3** at the TCB/HOPG interface. Image and packing parameters: 35.7 × 35.7 nm^2, V_S = –0.8 V, I_t = 21 pA, c = 10^{-6} M; a = (5.1 ± 0.2) nm, b = (4.9 ± 0.2) nm, $\gamma(a,b)$ = (81 ± 2)°, $\gamma(b,c)$ = (13 ± 2)°, $\gamma(a,d)$ = (3 ± 2)°. Red, blue, and white (black) lines indicate the unit cells, backbone (rod) directions, and HOPG main axis directions, respectively. The blue parallelograms in (b) represent the tiling indexed to **3**.

An overview STM image of **3** on HOPG is shown in Figure S9. In 87 % of the scan region, the packing as discussed in Figure 5 (Main Text) and Figure S7 is observed, while 13 % of the scan region remain uncovered (and appear medium bright without texture).

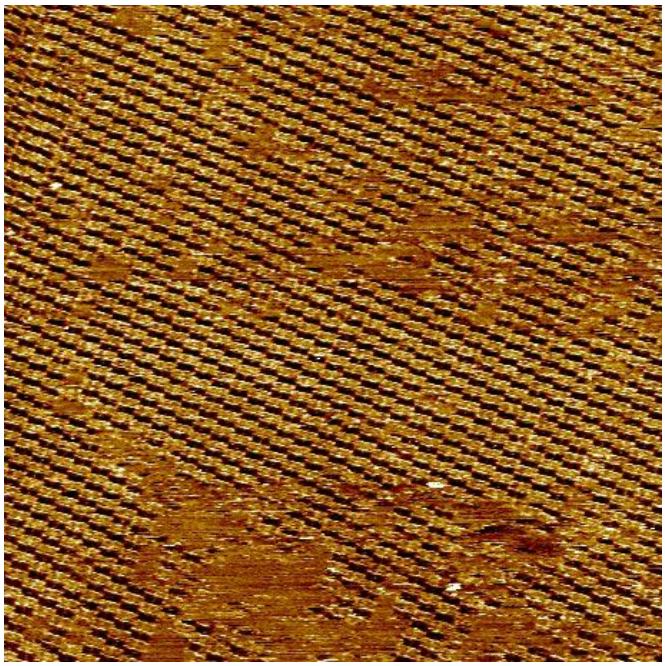


Figure S9. Overview STM image of **3** (180 × 180 nm^2 (internal scanner calibration), V_S = –0.7 V, I_t = 7 pA, c = 10^{-6} M).

3.4 STM images of 4

An enlarged reprint of Figure 6 (Main Text) is shown in Figure S10.

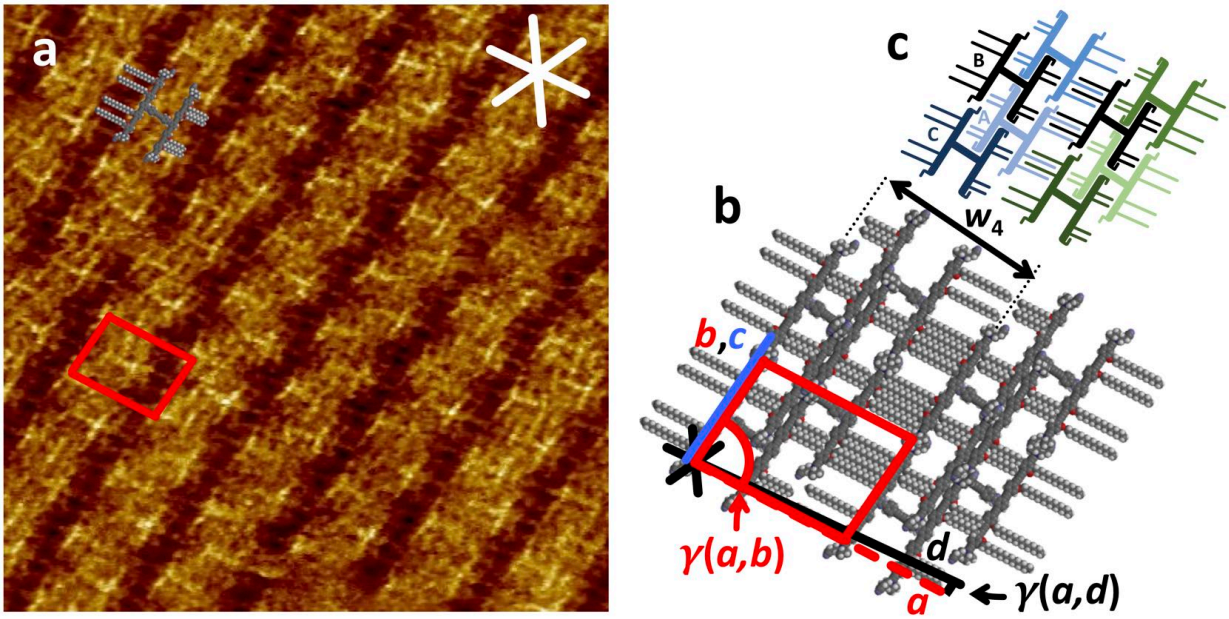


Figure S10. Reprint of Figure 6 (Main Text). (a) STM image, (b) supramolecular model, and (c) schematic model of **4** at the TCB/HOPG interface. Image and packing parameters: 39.2 × 39.2 nm^2, V_S = –1.0 V, I_t = 19 pA, c = 10^{-5} M; a = (6.5 ± 0.2) nm, b = (4.8 ± 0.2) nm, $\gamma(a,b)$ = (83 ± 2)°, $\gamma(a,d)$ = (2 ± 2)°, w_4 = (4.8 ± 0.2) nm. Red, blue, and white (black) lines indicate the unit cell, backbone (rod) directions, and HOPG main axis directions, respectively.

An overview STM image of **4** on HOPG is shown in Figure S11. In 73 % of the scan region, the packing as discussed in Figure 6 (Main Text) and Figure S9 is observed (with some disorder). Two domains with different orientations are distinguishable. However, 27 % of the scan region are covered by non-crystalline regions (despite the elevated annealing temperature) or have scan artefacts.

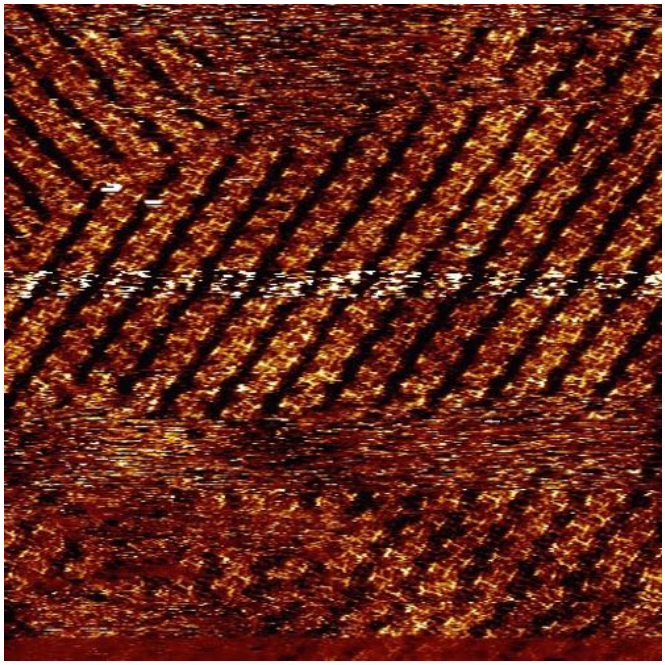


Figure S11. Overview STM image of **4** (100 × 100 nm^2 (internal scanner calibration), V_S = –1.0 V, I_t = 19 pA, c = 10^{-5} M).

3.5 Summary of packing parameters of 1–4

The lattice constants and additional packing parameters of self-assembled monolayers of **1**–**4** are summarized in Table S2.

compound	polym.	conc. / mol/L	*a* / nm	*b* / nm	$\gamma(a,b)$ / °	$\gamma(a,c)$ / °	$\gamma(b,c)$ / °	$\gamma(a,d_1)$ / °
1		10^{-7}...10^{-6}	5.1 ± 0.2	4.8 ± 0.2	60 ± 2	0 ± 2		90 ± 2
2	A	10^{-6}	5.3 ± 0.2	5.2 ± 0.2	60 ± 2	0 ± 2		87 ± 2
2	B	10^{-7}	6.0 ± 0.2	5.2 ± 0.2	84 ± 2	36 ± 2		24 ± 2
3		10^{-6}	5.1 ± 0.2	4.9 ± 0.2	81 ± 2		13 ± 2	3 ± 2
4		10^{-5}	6.5 ± 0.2	4.8 ± 0.2	83 ± 2		(0)	2 ± 2

Table S2. Summary of lattice constants and additional packing parameters of **1**–**4**.

4 Tesselation concept

In Figure S12, schematic models of supramolecular nanopatterns of **1**–**4** on HOPG, and related tilings that are indexed to the nanopatterns are shown. A rectangular tiling with tile width, w_1, is indexed to the self-assembled monolayer of **1** (Figure S12a). Increasing the length of the rod that bridges the two PEB sides (in **2**) leads to a similar pattern (Figure S12b) with increased tile width, w_2. In addition, an unexpected polymorph of **2** is observed where the backbones collapse (Figure S12c). One way to describe this nanopattern is by indexing a tiling of densely packed parallelograms (Figure S12c. In addition, a hexagonal tiling is indexed (Figure S12d). Green edges (that are perpendicular bisectors through the interdigitating alkoxy side chains, oriented with 60°/120° angles) indicate coordinating/binding sites, and red lines indicate non-coordinating/non-binding sides of the hexagons. While a "brick-like" tiling, that is not an edge-to-edge, tiling is indexed for **2** (with the polar CPDIPS end groups, Figure S12b), a tiling by parallelograms is indexed to **3** (with the biphenyl end groups, Figure S12e). Figure S12f visualizes the packing that was expected for H-shaped molecules **4** with short and long alkoxy side chains. However, the packing shown in Figure S12g was observed in the experiment.

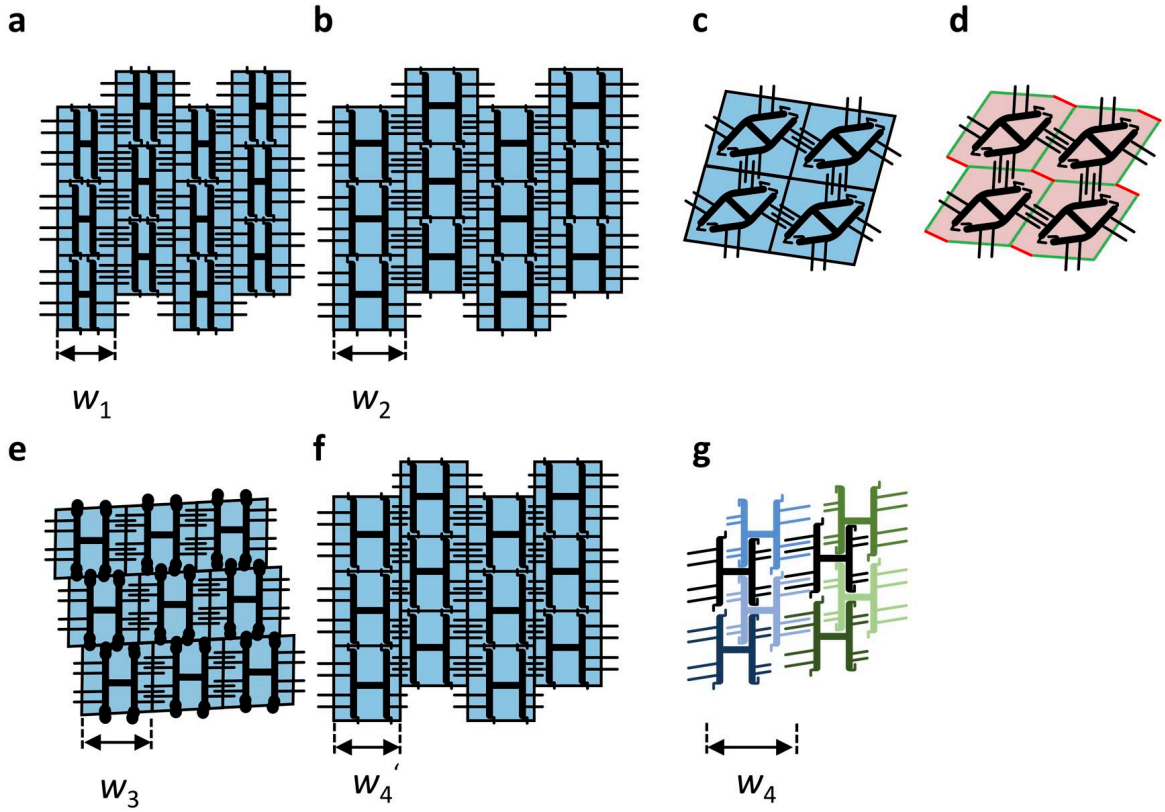


Figure S12. Supramolecular nanopatterns and indexed tilings. (a) **1**, (b) **2** (polymorph A), (c)–(d) **2** (polymorph B), (e) **3**, (f) **4** (expected), (g) **4** (observed).

Figure S13a shows a tiling with rectangles. Each vertex is surrounded by four rectangles. The tiling shown in Figure S13b is constructued starting from the tiling shown in Figure S13a by sliding the central row of rectangles relative to the other rows, which leads – according to Grünbaum and Shephard (Ref. [3]) – to the definition of α = (shift distance) / (tile length). Figure S13c shows the case of α = 0.5, which means that each long side of each rectangles overlaps with two halves of the long sides of two adjacent rectangles. Such a construction motive with running bonds is commonly used for brick walls, thus we call it "brick-like" tiling.

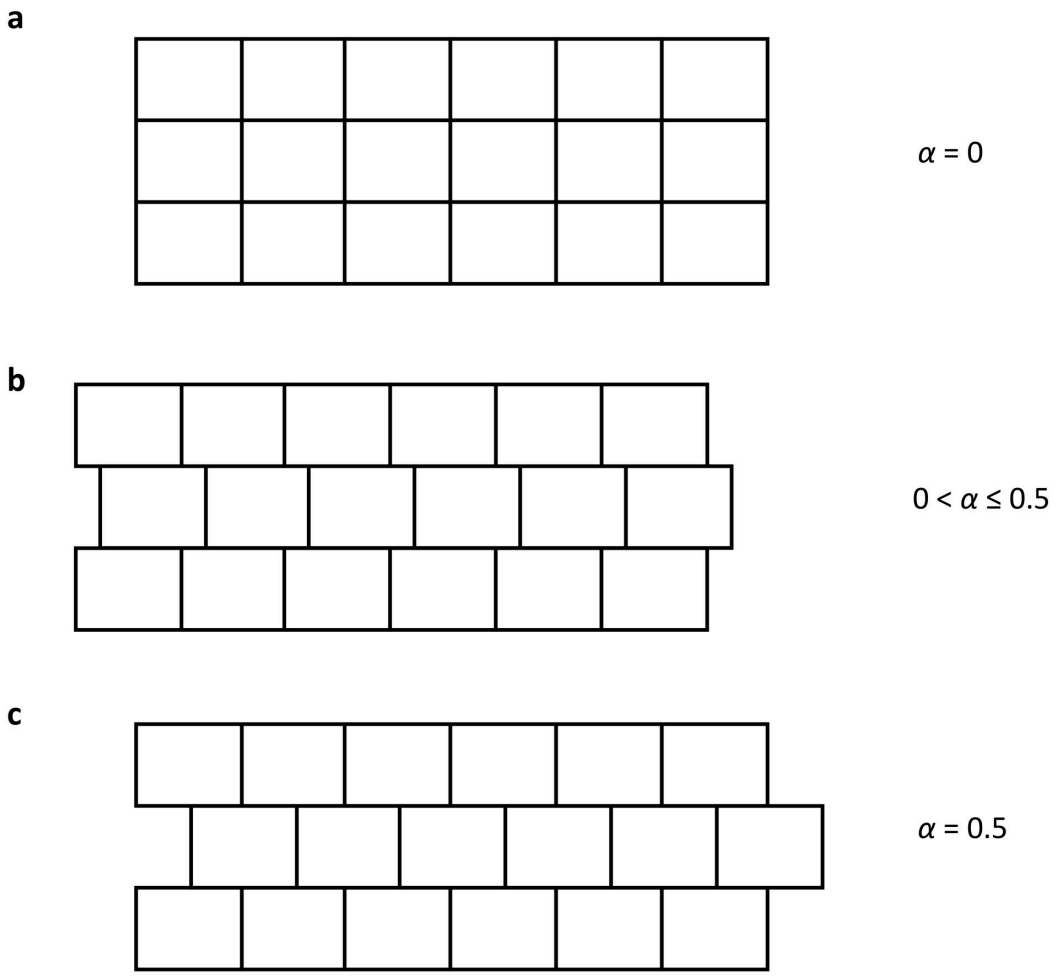


Figure S13. Tiling schemes with (a) full overlap of tiles (α = 1), (b) partial overlap (here: 0 < α < 0.5), and (c) overlap of each long tile side with half of the long tile sides of adjacent tiles (α = 0.5).

5 Syntheses

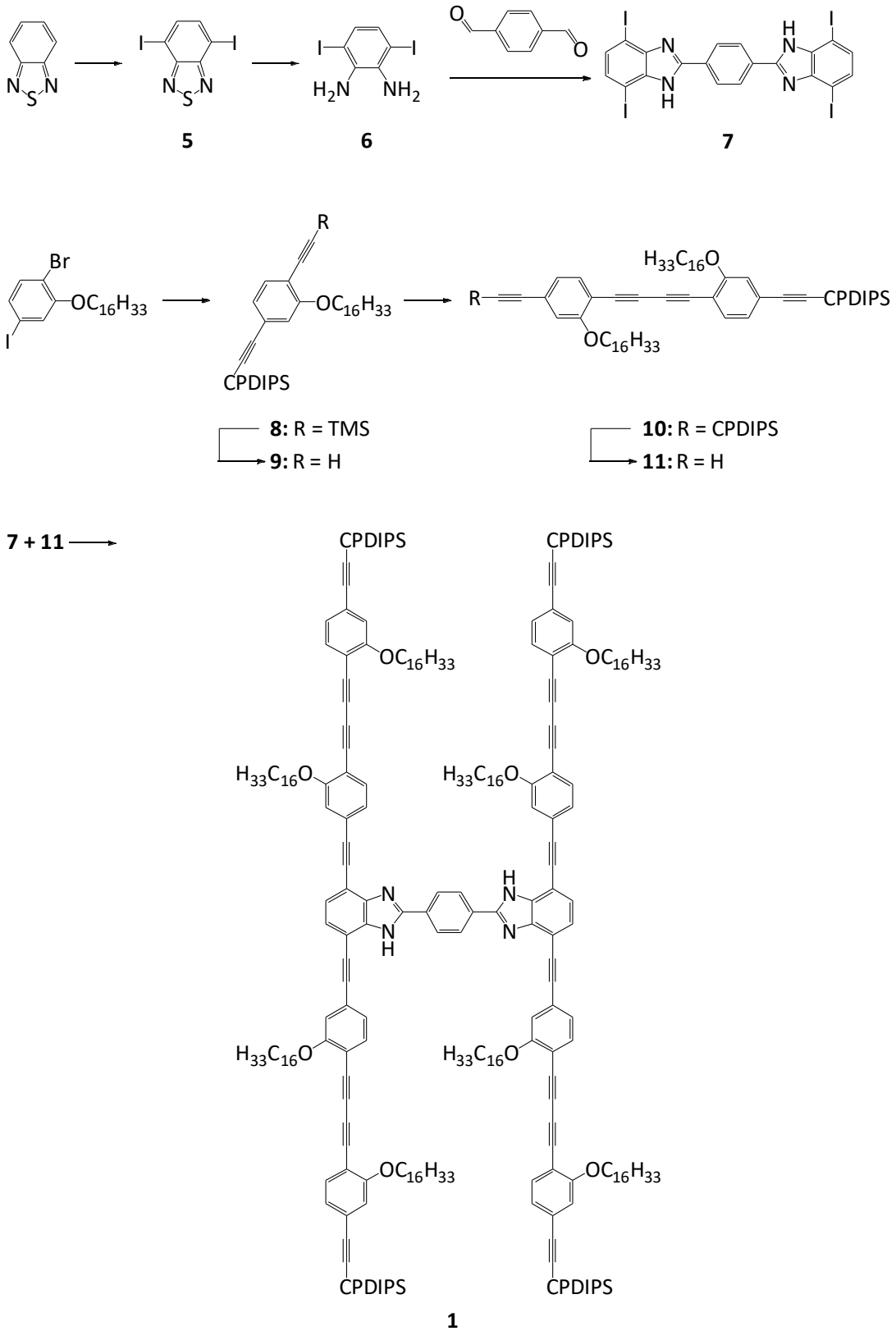
5.1 Synthesis of 1

Here we present the syntheses of H-shaped molecules based on benzimidazole and butadiynylene building blocks.

5.1.1 Synthetical strategy towards 1

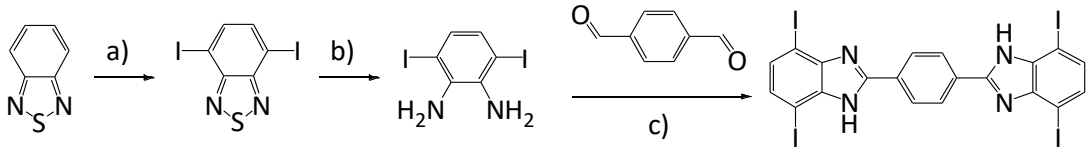
First we synthesized the bisbenzimdazole building block **7** using the previously reported compound **5**, which – in turn – was obtained from 2,1,3-benzothiadiazole.[4] Reduction with sodium borohydride in combination with cobalt(II)chloride hexahydrate yielded the diamine **6**.[5] After zirconium(IV)chloride catalyzed condensation with terephthalaldehyde the bisbenzimidazole building block **7** was obtained.[5] The butadiynylene building block was prepared by using the previously reported compound 1-bromo-2-hexadecyloxy-5-iodobenzene.[6] Palladium catalyzed *Sonogashira* coupling with (3-Cyanopropyl)diisopropylsilyl and TMS acetylene yielded the unsymmetrical bisacetylene **8**. Deprotection of the TMS group under basic conditions gave the monoprotected compound **9**. CuCl catalyzed *Glaser* reaction followed by statistical deprotection of **10** yielded the butadiynylene building block **11**. The H-shaped molecule **1** was then obtained by palladium catalyzed *Sonogashira* coupling of **7** and **11**.

Scheme S1. Synthetical strategy towards **1**.



5.1.2 Synthesis of the bisbenzimidazole building block 7

Scheme S2. Synthesis of **7**.



a) I_2, H_2SO_4 (30 % SO_3), 40 °C; b) $NaBH_4$, $CoCl_2$*$6H_2O$ cat., EtOH, THF, reflux; c) $ZrCl_4$ cat., $CHCl_3$, r. t.

5

Under an argon atmosphere, iodine (16.77 g, 66.09 mmol) was added to a solution of 2,1,3-benzothiadiazole (3.0 g, 22.03 mmol) in fuming sulfuric acid (30 % SO_3, 70 mL). The mixture was stirred at 40 °C for 4 h and at room temperature overnight. The reaction was quenched with ice (200 mL) and then diluted with dichloromethane. The organic layer was separated and washed with 10 % $NaHSO_3$ (aq), 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by recrystallization from acetone and **5** was obtained as a yellow solid (1.75 g, 20 %). Chemical formula: $C_6H_2I_2N_2S$, M = 387.96 g/mol. ^{1}H NMR (400 MHz, C*D*Cl_3,r.t.): δ [ppm] = 7.81 (s, 2H). ^{13}C NMR (101 MHz, C*D*Cl_3,r.t.): δ [ppm] = 153.9, 147.3, 139.8. MS (EI, 70 eV): *m/z* = 387.8 $[M]^{+\cdot}$, 260.9 $[M\text{-}I]^+$, 134.0 $[M\text{-}I_2]^+$, 126.9 $[I]^+$, 83.0 $[M\text{-}C_2H_3IO]^+$, 51.0 $[C_4H_3]^+$.

6

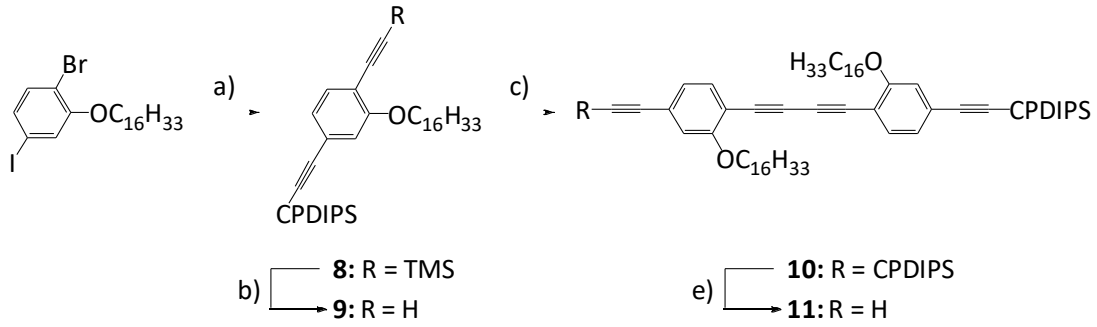
Under an argon atmosphere, small portions of sodium borohydride (0.54 g, 14.31 mmol) and cobalt(II) chloride hexahydrate (0.01 g, 0.05 mmol) were added at room temperature to a solution of **5** (1.85 g, 4.77 mmol) in ethanol (21 mL) and THF (7 mL). The mixture was stirred at reflux for 3 h, cooled down to room temperature and then diluted with diethyl ether. The organic layer was separated and washed with brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was unstable to air and used in the subsequent reaction without further purification (1.10 g, 64 %). Chemical formula: $C_6H_6I_2N_2$, M = 359.94 g/mol. ^{1}H NMR (400 MHz, C*D*Cl_3,r.t.): δ [ppm] = 6.90 (s, 2H), 3.88 (br. s, 4H). MS (EI, 70 eV): *m/z* = 359.9 $[M]^{+\cdot}$, 233.9 $[M\text{-}I+H]^+$, 76.0 $[C_6H_4]^+$.

7

Zirconium(IV) chloride (0.09 g, 0.40 mmol) was added to a solution of **6** (0.36 g, 0.99 mmol) and terephthalaldehyde (0.53 g, 3.95 mmol) in chloroform (80 mL). The mixture was stirred at room temperature overnight and then the solvent was evaporated. The crude product was purified by recrystallization from acetonitrile and obtained as a yellow solid (0.16 g, 38 %). Chemical formula: $C_{20}H_{10}I_4N_4$, M = 813.95 g/mol. ^{1}H NMR (400 MHz, DMSO-*d*$_6$,r.t.): δ [ppm] = 8.51 (s, 4H), 7.44 (s, 4H), 3.47 (br. s, 2H). MS (EI, 70 eV): *m/z* = 813.7 $[M]^{+\cdot}$, 687.9 $[M\text{-}I+H]^+$, 562.0 $[M\text{-}I_2+H_2]^+$, 460.0 $[M\text{-}C_6I_2N_2]^+$, 446.0 $[M\text{-}C_7H_2I_2N_2]^+$, 406.9 $[M\text{-}C_{10}H_5I_2N_2]^+$, 127.0 $[I]^+$.

5.1.3 Synthesis of the butadiynylene building block 11

Scheme S3. Synthesis of **11**.



a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, CPDIPS acetylene, TMS acetylene, piperidine, THF, r.t. – 50 °C; b) K_2CO_3, MeOH, THF, r. t.; c) CuCl, TMEDA, O_2, CH_2Cl_2, 30 °C; d) TBAF, H_2O, THF, r. t.

8

Under an argon atmosphere, CPDIPS acetylene (6.53 g, 31.5 mmol) was added to a solution of 1-bromo-2-hexadecyloxy-5-iodobenzene (15.70 g, 30.0 mmol), $PdCl_2(PPh_3)_2$ (0.32 g, 0.45 mmol), triphenylphosphane (0.32 g, 1.20 mmol) und copper(I) iodide (0.14 g, 0.75 mmol) in piperidine (80 mL). The mixture was stirred at room temperature overnight. Then, TMS acetylene (20.0 mL, 15.0 mmol) was added and the mixture was stirred at 50 °C overnight. After cooling down to room temperature the suspension was diluted with diethyl ether. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **8** as a yellowish oil (16.86 g, 91 %). Chemical formula: $C_{39}H_{65}ONSi_2$, M = 620.13 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.33 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.97 (dd, $^3J_{HH}$ =

7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 6.89 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 4.00 (t, $^3J_{HH}$ = 6.2 Hz, 2H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 1.90-1.79 (m, 4H), 1.55-1.48 (m, 2H), 1.37-1.26 (m, 24H), 1.14-1.05 (m, 14H), 0.90-0.81 (m, 5H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 159.9, 133.3, 124.2, 124.0, 119.7, 114.9, 113.5, 107.6, 100.8, 100.4, 90.9, 68.7, 31.9, 29.7, 29.7, 29.4, 29.3, 29.2, 26.0, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6, 0.1. MS (EI, 70 eV): *m/z* = 619.5 $[M]^{+\cdot}$, 576.5 $[M\text{-}C_3H_7]^+$, 548.4 $[M\text{-}C_5H_{11}]^+$, 326.2 $[M\text{-}C_{19}H_{37}Si]^+$, 257.1 $[M\text{-}C_{23}H_{42}OSi]^+$, 182.1 $[C_{11}H_{22}Si]^+$, 97.1 $[C_6H_9O]^+$, 83.1 $[C_6H_{11}]^+$, 73.1 $[C_3H_9Si]^+$, 57.1 $[C_4H_9]^+$.

9

Under an argon atmosphere, potassium carbonate (4.03 g, 29.12 mmol) was added to a solution of **8** (9.03 g, 14.56 mmol) in THF (120 mL) and methanol (120 mL). The mixture was stirred at room temperature for 3 h and then diluted with diethyl ether. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **9** as a yellowish oil (7.49 g, 94 %). Chemical formula: $C_{30}H_{45}ONSi$, M = 463.78 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.37 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.00 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 6.93 (d, $^4J_{HH}$ = 1.2 Hz, 1H), 4.03 (t, $^3J_{HH}$ = 6.6 Hz, 2H), 3.33 (s, 1H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 1.91-1.78 (m, 4H), 1.53-1.45 (m, 2H), 1.34-1.25 (m, 24H), 1.12-1.05 (m, 14H), 0.90-0.81 (m, 5H). ^{13}C NMR (76 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 159.9, 133.8, 124.4, 124.2, 119.7, 115.0, 112.4, 107.4, 91.1, 82.6, 79.7, 68.9, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.0, 25.9, 22.7, 21.2, 20.8, 18.2, 17.9, 14.1, 11.7, 9.6. MS (EI, 70 eV): *m/z* = 547.4 $[M]^{+\cdot}$, 504.4 $[M\text{-}C_3H_7]^+$.

10

Under an argon atmosphere, copper(I) chloride (1.38 g, 13.91 mmol) and TMEDA (2.1 mL, 13.91 mmol) were added to a solution of **9** (7.62 g, 13.91 mmol) in dichloromethane (430 mL). With a small membrane pump, a steady flow of air was piped through the solution and the mixture was stirred at 30 °C for 4 h. After cooling down to room temperature the suspension was diluted with dichloromethane. The organic layer was separated and washed with water, 25 % NH_3, 10 % HCl and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **10** as a yellowish oil (6.71 g, 88 %). Chemical formula: $C_{72}H_{112}N_2O_2Si_2$, M = 1093.87 g/mol. ^{1}H NMR (300 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.38 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.00 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 6.92 (d, $^4J_{HH}$ = 1.2 Hz,

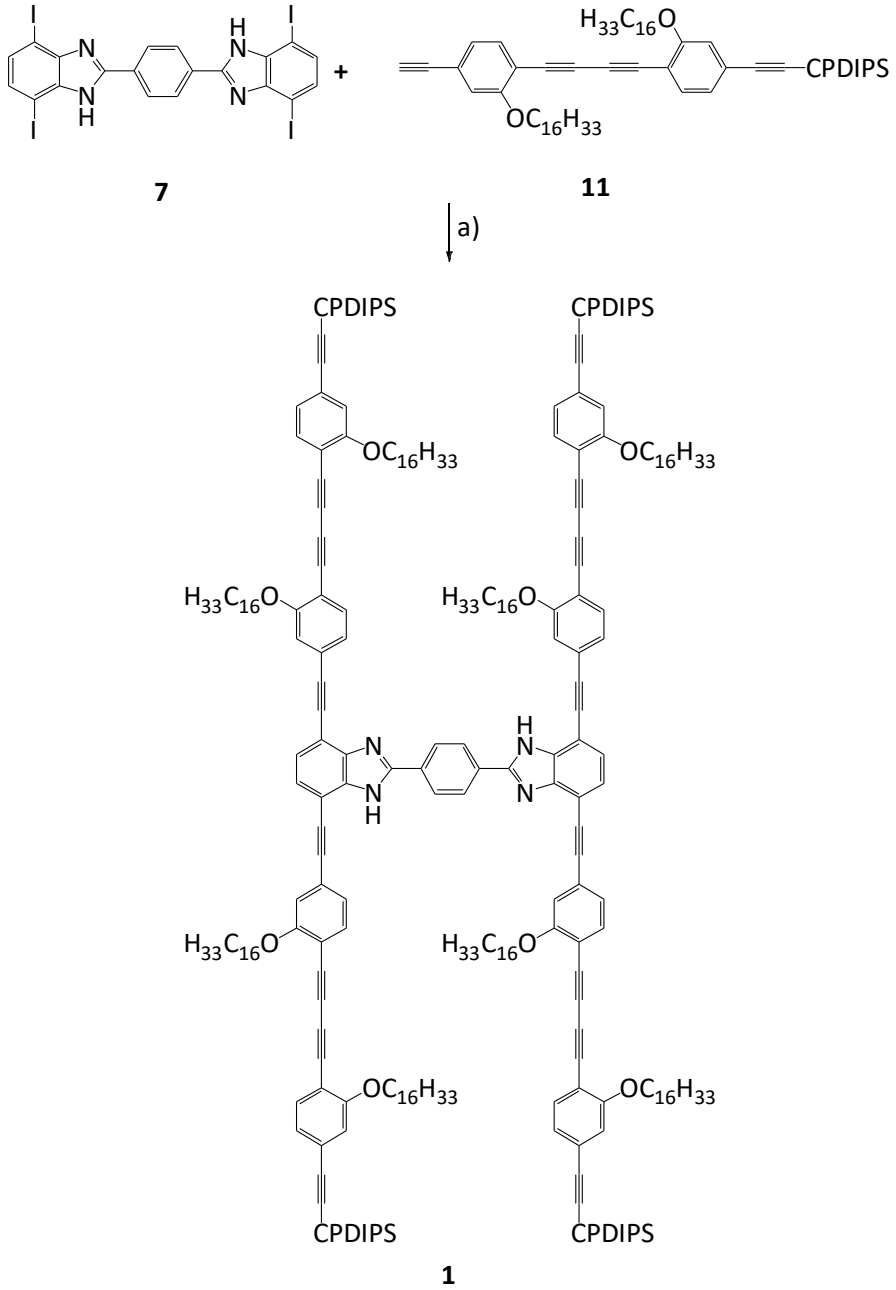
2H), 4.03 (t, $^{3}J_{HH}$ = 6.6 Hz, 4H), 2.43 (t, $^{3}J_{HH}$ = 6.8 Hz, 4H), 1.92-1.82 (m, 8H), 1.53-1.46 (m, 4H), 1.39-1.23 (m, 48H), 1.12-1.09 (m, 28H), 0.89-0.82 (m, 10H). ^{13}C NMR (76 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 134.0, 124.6, 124.4, 119.7, 115.0, 114.9, 112.5, 107.4, 91.8, 79.5, 79.1, 31.9, 29.7, 29.7, 29.6, 29.4, 29.3, 29.0, 25.9, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6. MS (MALDI-TOF, DCTB): *m/z* = 1092.9 $[M]^{+}$.

11

Under an argon atmosphere, TBAF (1M in THF, 6.1 mL, 6.10 mmol) was added to a solution of **10** (6.71 g, 6.13 mmol) in THF (480 mL) and water (36 mL) at 0 °C. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 4.5 h. The reaction was quenched by addition of water and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **7** as a yellow solid (1.10 g, 20 %). Chemical formula: $C_{62}H_{93}NO_2Si$, M = 912.52 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.40 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.39 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.02 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H), 7.00 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.97 (d, $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.92 (d, $^{4}J_{HH}$ = 1.2 Hz, 1H), 4.04 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H), 4.02 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H), 3.17 (s, 1H), 2.43 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H), 1.91-1.81 (m, 6H), 1.53-1.46 (m, 4H), 1.38-1.23 (m, 48H), 1.12-1.08 (m, 14H), 0.92-0.82 (m, 8H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.5, 134.1, 134.0, 124.6, 124.3, 124.2, 123.8, 119.7, 115.3, 115.0, 112.6, 112.5, 107.4, 91.8, 83.3, 79.6, 79.5, 79.1, 79.0, 78.9, 69.1, 69.0, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.0, 28.9, 25.9, 25.9, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6. MS (EI, 70 eV): *m/z* = 911.6 $[M]^{+\cdot}$, 700.5 $[M\text{-}C_{15}H_{31}]^{+}$.

5.1.4 Synthesis of 1

Scheme S4. Synthesis of **1**.



a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, piperidine, THF, 40 °C.

1

Under an argon atmosphere, a solution of **11** (0.12 mg, 0.13 mmol) in THF (5 mL) was added to a solution of **7** (0.03 g, 0.03 mmol), $PdCl_2(PPh_3)_2$ (0.004 mg, 0.006 mmol), triphenylphosphane (0.003 g, 0.01 mmol) und copper(I) iodide (0.002 mg, 0.01 mmol) in piperidine (30 mL). The mixture was stirred at 40 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent

was evaporated. The crude product was purified by *rec*-GPC and yielded **1** as a yellow solid (0.1 g, 10 %). Chemical formula: $C_{268}H_{378}N_8O_8Si_4$, M = 3952.36 g/mol. ^{1}H NMR (500 MHz, CD_2Cl_4, 363 K): δ [ppm] = 8.29 (s, 4H), 7.47 (s, 4H), 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 4H), 7.35 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.20-7.13 (m, 8H), 6.98 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, 4H), 6.91 (d, $^4J_{HH}$ = 1.5 Hz, 4H), 4.10 (t, $^3J_{HH}$ = 6.5 Hz, 8H), 4.03 (t, $^3J_{HH}$ = 6.5 Hz, 8H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 8H), 1.88-1.79 (m, 24H), 1.54-1.47 (m, 16H), 1.46-1.41 (m, 16H), 1.41-1.35 (m, 16H), 1.34-1.20 (m, 162H), 1.11-1.07 (m, 56H), 0.86-0.80 (m, 32H). MS (MALDI-TOF, DCTB): *m/z* = 4701.9 $[M+3DCTB]^+$, 4452.2 $[M+2DCTB]^+$, 4202.4 $[M+DCTB]^+$, 3952.4 $[M]^+$, 3727.6 $[M-C_{16}H_{32}]^+$, 3502.5 $[M-C_{32}H_{65}]^+$.

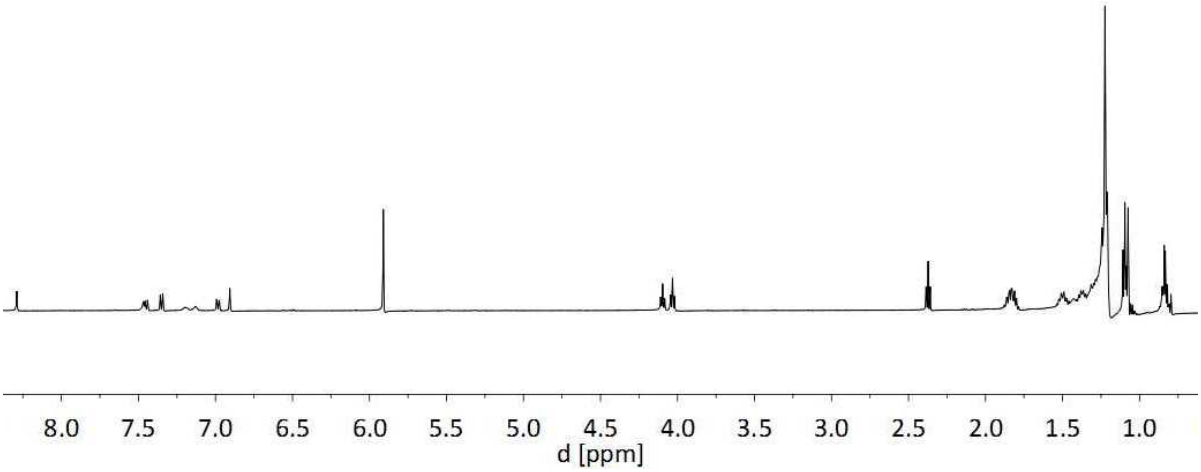


Figure S14. ^{1}H NMR of **1**.

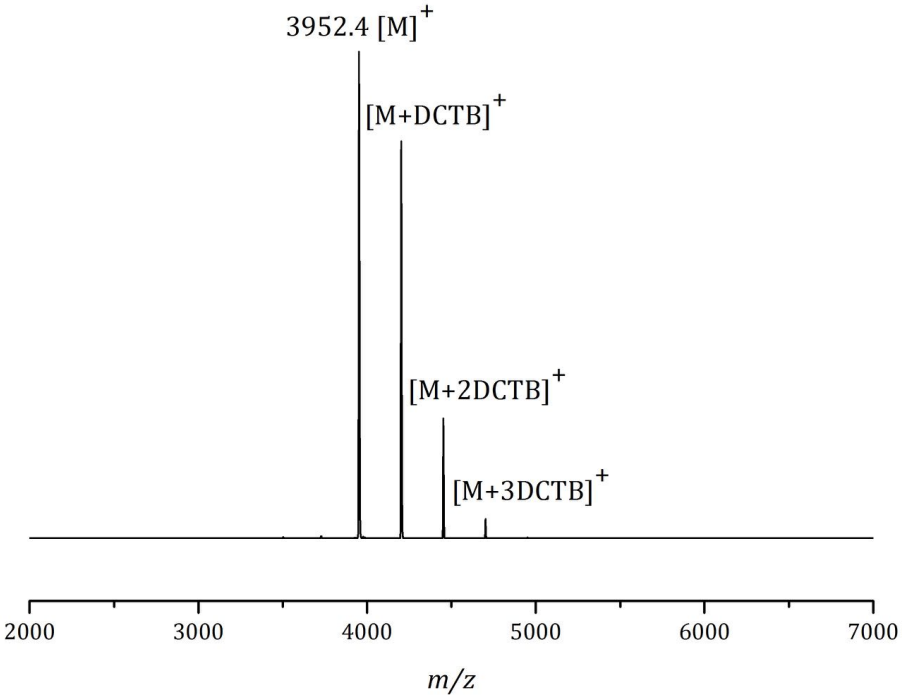


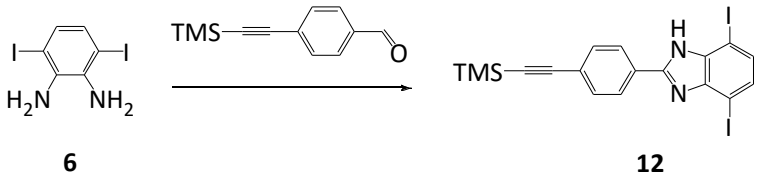
Figure S15. MALDI spectrum of **1** (matrix: DCTB).

5.2 Synthesis of 2 and 4

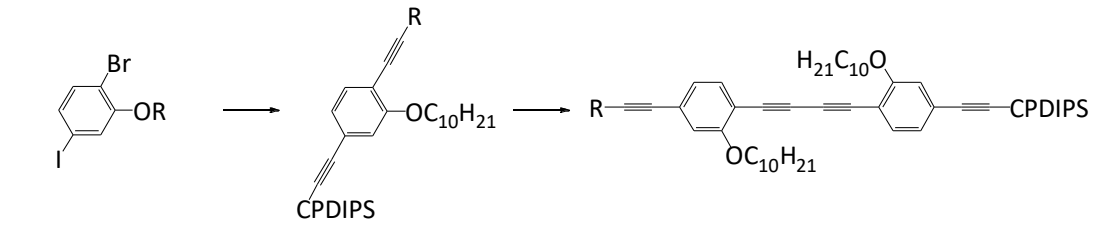
5.2.1 Synthetical strategy towards 2 and 4

Here we present the syntheses of an unsymmetrical and the two corresponding symmetrical H-shaped molecules based on two benzimidazole building blocks connected by a butadiynylene unit and butadiynylene building blocks that are functionalized with either hexadecyloxy or decyloxy side chains. First we synthesized the benzimidazole compound **12** *via* zirconium(IV)chloride catalysed condensation, this time with 4-[trimethylsilyl)-ethynyl)]benzaldehyde. The butadiynylene building block was prepared analogously to **11** by using the previously reported compound 2-bromo-4-iodophenol.[6] Etherification with decyloxy groups gave compound **13** which was then used in a palladium catalyzed *Sonogashira* coupling with (3-Cyanopropyl)diisopropylsilyl and TMS acetylene to yield the unsymmetrical bisacetylene **14**. Deprotection of the TMS group under basic conditions gave the monoprotected compound **15**. CuCl catalyzed *Glaser* reaction followed by statistical deprotection of **16** yielded the butadiynylene building block **17**. The T-shaped building blocks **18a** and **18b** with either hexadecyloxy or decyloxy side chains were then obtained by *Sonogashira* coupling of **12** and either **11** or **17**, respectively. After deprotection of the TMS group under basic conditions the deprotected T-shaped building blocks **19a** and **19b** were used in a statistical CuCl catalyzed *Glaser* coupling to give the H-shaped molecules **2**, **4**, **23**

Scheme S5. Synthetical strategy towards **19a**/**b**.



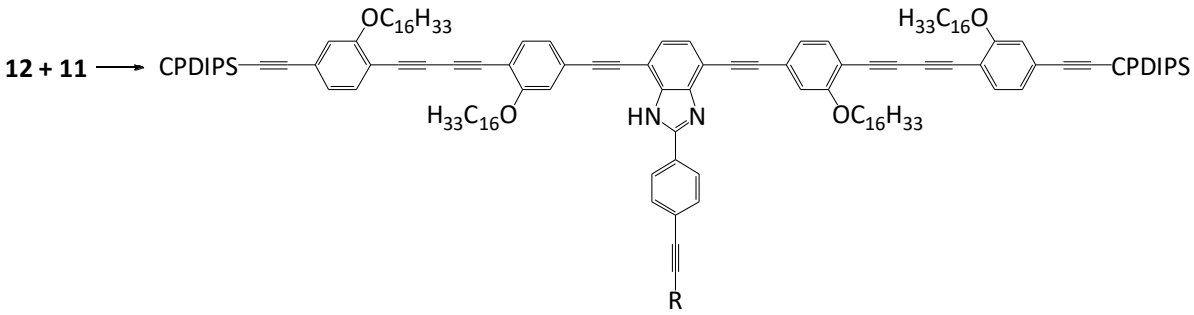
6 **12**



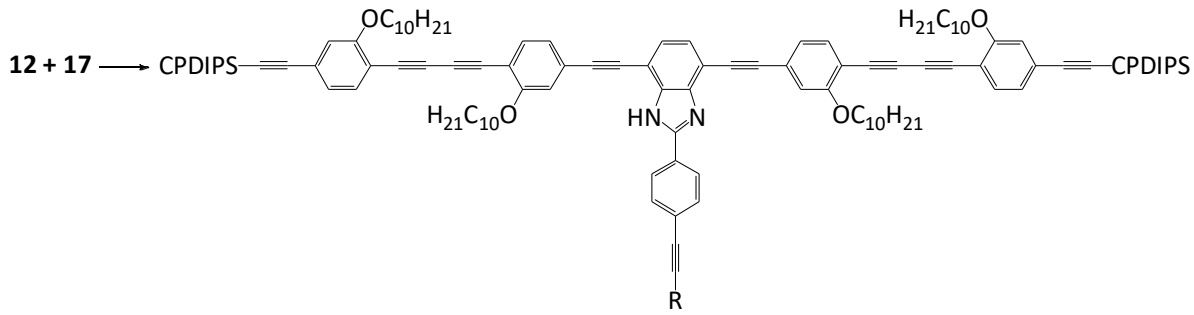
R = H → **13:** R = $C_{10}H_{21}$

14: R = TMS → **15:** R = H

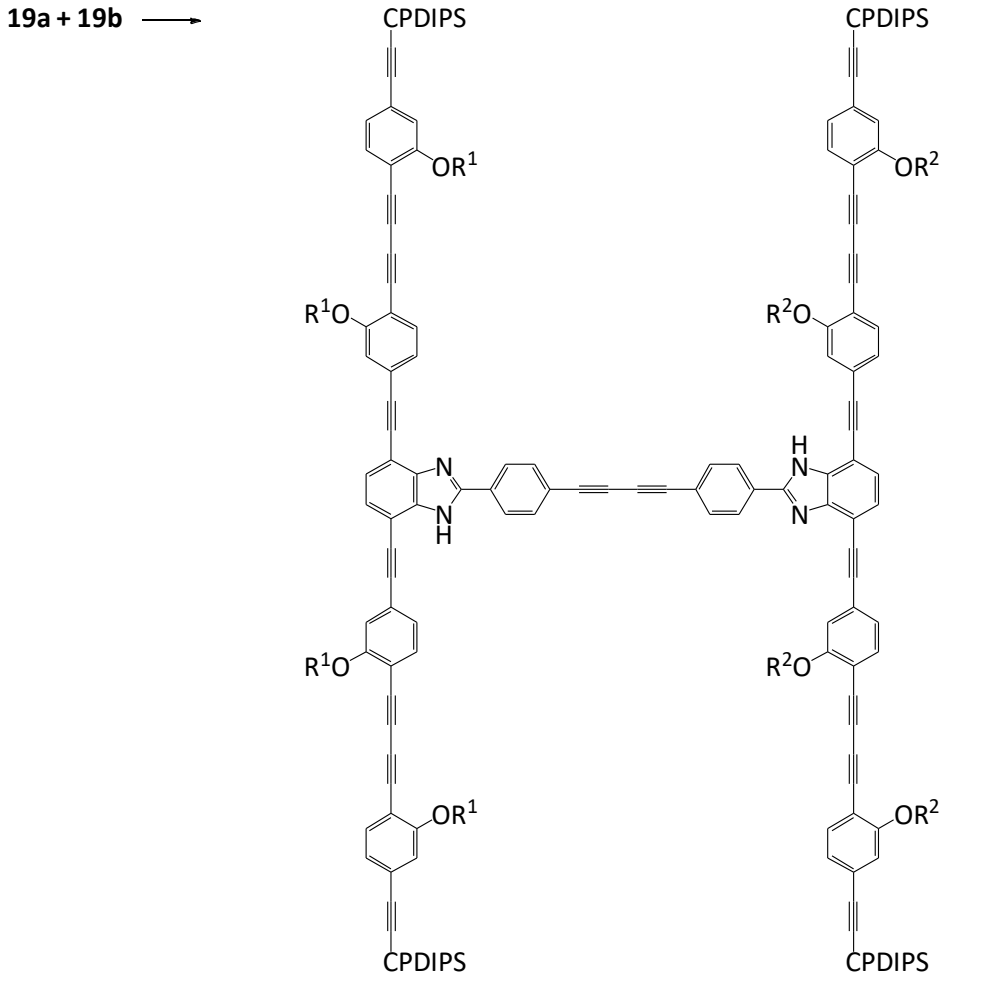
16: R = CPDIPS → **17:** R = H



18a: R = TMS → **19a:** R = H



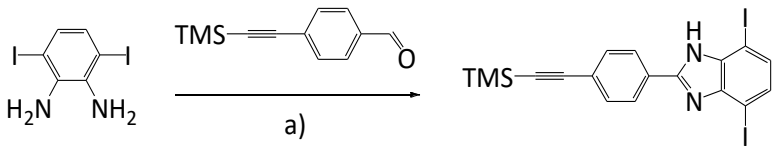
18b: R = TMS → **19b:** R = H



2: $R^1 = R^2 = C_{16}H_{33}$, **4:** $R^1 = C_{16}H_{33}$, $R^2 = C_{10}H_{21}$, **23:** $R^1 = R^2 = C_{10}H_{21}$

5.2.2 Synthesis of the benzimidazole building block 12

Scheme S6. Synthesis of **12**.



6 **12**

a) $ZrCl_4$ cat., $CHCl_3$, r. t.

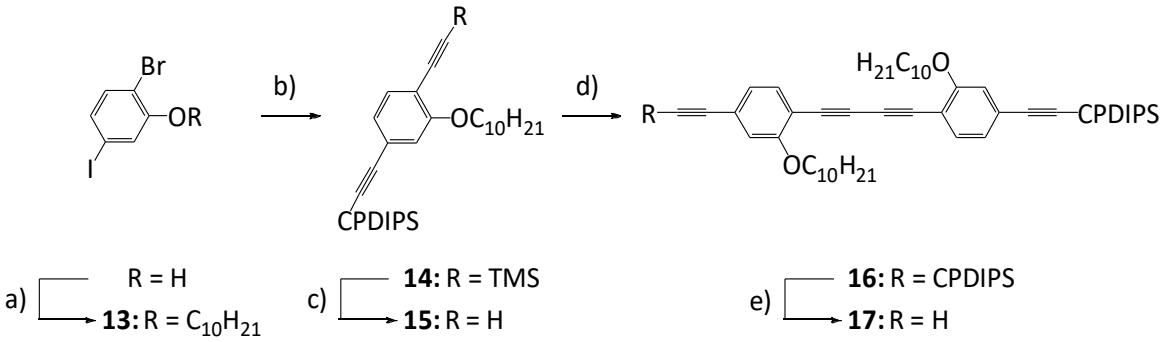
12

Zirconium(IV) chloride (0.05 g, 0.20 mmol) was added to a solution of **6** (0.37 g, 1.03 mmol) and 4-[trimethylsilyl)ethynyl)]benzaldehyde (0.41 g, 2.03 mmol) in chloroform (100 mL). The mixture was stirred at room temperature overnight, the solvent was evaporated and the crude product diluted with ethyl acetate. The organic layer was separated and washed with water and

brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **12** as a yellowish solid (0.41 g, 73 %). Chemical formula: $C_{18}H_{16}I_2N_2Si$, M = 542.23 g/mol. ^{1}H NMR (300 MHz, CD_2Cl_2,r.t.): δ [ppm] = 9.74 (br. s, 1H), 8.03 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.57 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.40 (s, 2H), 0.28 (s, 9H). ^{13}C NMR (76 MHz, CD_2Cl_2,r.t.): δ [ppm] = 162.9, 150.9, 133.9, 133.0, 132.5, 129.9, 129.1, 127.3, 126.2, 104.6, 97.8, 0.1. MS (EI, 70 eV): *m/z* = 542.0 $[M]^{+\cdot}$, 526.9 $[M\text{-}CH_3]^+$, 416.1 $[M\text{-}I\text{+}H]^+$, 400.0 $[M\text{-}CH_3I]^+$, 288.9 $[M\text{-}I_2\text{+}H]^+$, 273.1 $[M\text{-}CH_3I_2]^+$, 200.0 $[M\text{-}C_6H_2I_2N]^+$, 187.1 $[M\text{-}C_6HI_2N_2]^+$.

5.2.3 Synthesis of the butadiynylene building block 17

Scheme S7. Synthesis of **17**.



a) KI, K_2CO_3, 1-bromodecane, DMF, 60 °C; b) $PdCl_2(PPh_3)_2$, PPh_3, CuI, CPDIPS acetylene, TMS acetylene, piperidine, THF, r.t. – 50 °C; c) K_2CO_3, MeOH, THF, r. t.; d) CuCl, TMEDA, O_2, CH_2Cl_2, 30 °C; e) TBAF, H_2O, THF, r. t.

13

Under an argon atmosphere, potassium carbonate (8.16 g, 59.02 mmol), potassium iodide (0.25 g, 1.48 mmol) and 1-bromodecane (4.0 mL, 19.28 mmol) were added to a solution of 2-bromo-4-iodophenol (4.41 g, 14.75 mmol) in DMF (100 mL). The mixture was stirred at 60 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane as eluent and yielded **13** as a white solid (6.33 g, 98 %). Chemical formula: $C_{16}H_{24}BrIO$, M = 439.18 g/mol. ^{1}H NMR (400 MHz, $CDCl_3$,r.t.): δ [ppm] = 7.22 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.15 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 7.13 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ =1.8 Hz, 1H), 3.98 (t, $^3J_{HH}$ = 6.4 Hz, 2H), 1.86-1.79 (m, 2H), 1.52-1.45 (m, 2H), 1.38-1.20 (m, 12H), 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$,r.t.): δ [ppm] = 156.1, 134.4, 130.6, 122.3,

112.3, 92.3, 69.5, 31.9, 29.5, 29.3, 29.3, 28.9, 25.9, 22.7, 14.1. MS (EI, 70 eV): *m/z* = 438.0 $[M]^{+\cdot}$, 297.9 $[M\text{-}C_{10}H_{20}]^{+}$, 97.1 $[C_6H_9O]^{+}$, 85.1 $[C_6H_{13}]^{+}$, 69.1 $[C_4H_5O]^{+}$, 55.1 $[C_4H_7]^{+}$.

14

Under an argon atmosphere, CPDIPS acetylene (3.08 g, 14.87 mmol) was added to a solution of **13** (6.22 g, 14.16 mmol), $PdCl_2(PPh_3)_2$ (0.15 g, 0.21 mmol), triphenylphosphane (0.15 g, 0.57 mmol) und copper(I) iodide (0.07 g, 0.35 mmol) in piperidine (50 mL) and THF (100 mL). The mixture was stirred at room temperature overnight. Then, TMS acetylene (9.8 mL, 70.82 mmol) was added and the mixture was stirred at 50 °C overnight. After cooling down to room temperature the suspension was diluted with diethyl ether. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **14** as a yellowish oil (6.57 g, 87 %). Chemical formula: $C_{33}H_{53}ONSi_2$, M = 535.96 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.33 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.98 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.89 (s, 1H), 4.01 (t, $^3J_{HH}$ = 6.2 Hz, 2H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 1.90-1.79 (m, 4H), 1.56-1.49 (m, 2H), 1.42-1.22 (m, 12H), 1.18-1.05 (m, 15H), 0.90-0.81 (m, 4H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 159.8, 133.2, 124.2, 124.0, 119.7, 115.0, 113.5, 107.5, 100.8, 100.4, 90.9, 68.7, 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6, 0.1. MS (EI, 70 eV): *m/z* = 535.4 $[M]^{+\cdot}$, 492.3 $[M\text{-}C_3H_7]^{+}$, 464.3 $[M\text{-}C_5H_{11}]^{+}$, 83.1 $[C_6H_{11}]^{+}$, 73.1 $[C_3H_9Si]^{+}$.

15

Under an argon atmosphere, potassium carbonate (3.34 g, 24.14 mmol) was added to a solution of **14** (6.47 g, 12.07 mmol) in THF (145 mL) and methanol (145 mL). The mixture was stirred at room temperature for 3 h and then diluted with diethyl ether. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. **15** was obtained without further purification as a yellowish oil (5.02 g, 90 %) . Chemical formula: $C_{30}H_{45}ONSi$, M = 463.78 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.36 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 6.92 (s, 1H), 4.03 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 3.33 (s, 1H), 2.43 (t, $^3J_{HH}$ = 9.2 Hz, 2H), 1.90-1.80 (m, 4H), 1.52-1.45 (m, 2H), 1.40-1.18 (m, 12H), 1.12-1.02 (m, 15H), 0.90-0.82 (m, 4H). MS (EI, 70 eV): *m/z* = 463.4 $[M]^{+\cdot}$, 420.4 $[M\text{-}C_3H_7]^{+}$.

16

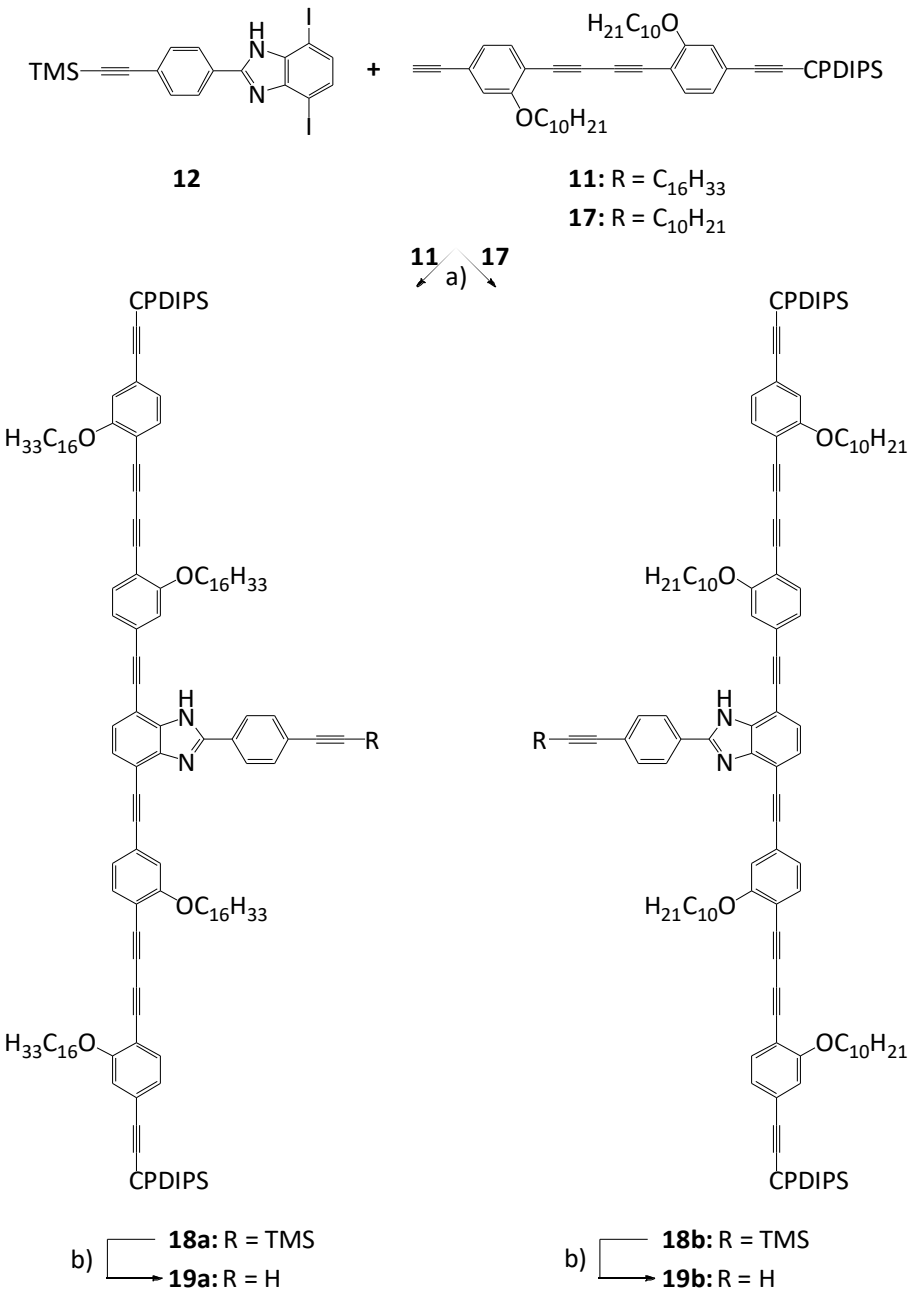
Under an argon atmosphere, copper(I) chloride (1.13 g, 11.45 mmol) and TMEDA (1.8 mL, 11.92 mmol) were added to a solution of **15** (4.99 g, 11.45 mmol) in dichloromethane (360 mL). With a small membrane pump, a steady flow of air was piped through the solution and the mixture was stirred at 30 °C for 4 h. After cooling down to room temperature the suspension was diluted with dichloromethane. The organic layer was separated and washed with water, 25 % NH_3, 10 % HCl and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:1) as eluent and yielded **16** as a yellow oil (3.46 g, 65 %). Chemical formula: $C_{60}H_{88}N_2O_2Si_2$, M = 925.55 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.38 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 6.92 (d, $^4J_{HH}$ = 0.8 Hz, 2H), 4.03 (t, $^3J_{HH}$ = 6.6 Hz, 4H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 1.90-1.82 (m, 8H), 1.54-1.47 (m, 4H), 1.39-1.20 (m, 24 H), 1.12-1.07 (m, 28H), 0.89-0.82 (m, 10H). ^{13}C NMR (101 MHz, C*D*Cl$_3$, r.t.): δ [ppm] = 160.6, 134.0, 124.6, 124.3, 119.7, 115.0, 112.5, 107.4, 91.8, 79.5, 79.0, 69.0, 31.9, 29.6, 29.5, 29.3, 29.3, 29.0, 25.9, 22.7, 21.2, 20.8, 18.2, 17.9, 14.1, 11.7, 9.6. MS (EI, 70 eV): *m/z* = 924.6 $[M]^{+\cdot}$, 881.5 $[M\text{-}C_3H_7]^+$, 797.5 $[M\text{-}C_6H_{13}SiN]^+$, 83.1 $[C_6H_{11}]^+$, 55.1 $[C_4H_7]^+$.

17

Under an argon atmosphere, TBAF (1M in THF, 3.80 mL, 3.80 mmol) was added to a solution of **16** (3.46 g, 3.74 mmol) in THF (300 mL) and water (22.5 mL) at 0 °C. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 4 h. The reaction was quenched by addition of water and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (3:2) as eluent and yielded **17** as a yellow oil (1.06 g, 38 %). Chemical formula: $C_{50}H_{69}NO_2Si$, M = 744.19 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.40 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.02 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.00 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 6.97 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 6.92 (d, $^4J_{HH}$ = 0.8 Hz, 1H), 4.05-4.00 (m, 4H), 3.18 (s, 1H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 1.90-1.81 (m, 6H), 1.54-1.45 (m, 4H), 1.37-1.18 (m, 24H), 1.12-1.07 (m, 14H), 0.87-0.82 (m, 8H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.5, 134.1, 134.0, 124.6, 124.4, 124.2, 123.8, 119.7, 115.3, 115.0, 112.6, 112.4, 107.4, 91.8, 83.3, 79.5, 79.1, 79.0, 78.9, 69.1, 69.0, 31.9, 29.6, 29.6, 29.3, 29.3, 29.0, 28.9, 25.9, 25.9, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6. MS (EI, 70 eV): *m/z* = 743.5 $[M]^{+\cdot}$, 700.5 $[M\text{-}C_3H_7]^+$, 616.4 $[M\text{-}C_6H_{13}SiN]^+$, 83.1 $[C_6H_{11}]^+$, 69.1 $[C_4H_5O]^+$.

5.2.4 Synthesis of the T-shaped building blocks 19a and 19b

Scheme S8. Synthesis of **19a** and **19b**.



a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, piperidine, 40 °C; b) K_2CO_3, MeOH, THF, r. t.

18a

Under an argon atmosphere, **11** (0.19 g, 0.20 mmol) was added to a solution of **12** (0.05 g, 0.09 mmol), $PdCl_2(PPh_3)_2$ (0.01 g, 0.01 mmol), triphenylphosphane (0.01 g, 0.04 mmol) and copper(I) iodide (0.004 g, 0.02 mmol) in piperidine (20 mL). The mixture was stirred at 40 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine,

dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:1 → 2:3) as eluent and yielded **18a** as a yellow solid (0.16 g, 83 %). Chemical formula: $C_{142}H_{200}N_4O_4Si_3$, M = 2111.44 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.10 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.48 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.41-7.38 (m, 6H), 7.03-6.93 (m, 8H), 4.05 (t, $^3J_{HH}$ = 6.6 Hz, 4H), 3.96 (t, $^3J_{HH}$ = 6.6 Hz, 4H), 2.42 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.89-1.80 (m, 12H), 1.54-1.45 (m, 8H), 1.37-1.19 (m, 97H), 1.12-1.07 (m, 28H), 0.89-0.81 (m, 16H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.5, 151.9, 134.0, 134.0, 132.4, 127.0, 126.8, 125.4, 124.6, 124.4, 123.9, 119.7, 115.0, 114.7, 112.5, 112.2, 107.4, 104.2, 97.1, 95.3, 91.7, 79.7, 79.3, 79.1, 69.0, 69.0, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.0, 29.0, 25.9, 25.9, 22.7, 21.2, 20.7, 18.2, 17.9, 14.1, 11.7, 9.6, 0.2. MS (MALDI-TOF, DCTB): *m/z* = 3360.3 [M+5DCTB]$^+$, 3109.1 [M+4DCTB]$^+$, 2860.0 [M+3DCTB]$^+$, 2609.8 [M+2DCTB]$^+$, 2359.6 [M+DCTB]$^+$, 2109.4 [M]$^+$.

18b

Under an argon atmosphere, **17** (0.19 g, 0.20 mmol) was added to a solution of **12** (0.05 g, 0.09 mmol), $PdCl_2(PPh_3)_2$ (0.01 g, 0.01 mmol), triphenylphosphane (0.01 g, 0.04 mmol) and copper(I) iodide (0.004 g, 0.02 mmol) in piperidine (20 mL). The mixture was stirred at 40 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:1 → 2:3) as eluent and yielded **18b** as a yellow solid (0.12 g, 70 %). Chemical formula: $C_{118}H_{152}N_4O_4Si_3$, M = 1774.79 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.09 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.41-7.37 (m, 6H), 7.03-6.93 (m, 8H), 4.04 (t, $^3J_{HH}$ = 6.6 Hz, 4H), 3.95 (t, $^3J_{HH}$ = 6.6 Hz, 4H), 2.41 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.89-1.80 (m, 12H), 1.54-1.45 (m, 8H), 1.37-1.19 (m, 49H), 1.12-1.07 (m, 28H), 0.89-0.81 (m, 16H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.5, 152.0, 134.0, 133.9, 132.3, 128.7, 127.0, 126.7, 125.3, 124.6, 124.4, 123.9, 119.7, 115.0, 114.6, 112.4, 112.2, 107.4, 104.2, 97.0, 95.3, 91.7, 79.6, 79.3, 79.1, 69.0, 68.9, 31.9, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 29.0, 28.9, 25.9, 25.9, 22.6, 21.2, 20.7, 8.2, 17.9, 14.1, 11.7, 9.5, 0.2. MS (MALDI-TOF, DCTB): *m/z* = 2523.6 [M+3DCTB]$^+$, 2273.4 [M+2DCTB]$^+$, 2023.2 [M+DCTB]$^+$, 1773.1 [M]$^+$.

19a

Under an argon atmosphere, potassium carbonate (0.11 g, 0.78 mmol) was added to a solution of **18a** (0.33 g, 0.16 mmol) in THF (10 mL) and methanol (10 mL). The mixture was stirred at room temperature for 3 h and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:2) as eluent and yielded **19a** as a yellow solid (0.15 g, 50%). Chemical formula: $C_{139}H_{192}N_4O_4Si_2$, M = 2039.26 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.13 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.54 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.43-7.39 (m, 6H), 7.08-7.00 (m, 6H), 6.93 (d, $^4J_{HH}$ = 1.2 Hz, 2H), 4.04 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 4.00 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 3.20 (s, 1H), 2.42 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 1.90-1.82 (m, 12H), 1.54-1.46 (m, 8H), 1.37-1.19 (m, 97H), 1.12-1.07 (m, 28H), 0.89-0.82 (m, 16H). MS (MALDI-TOF, DCTB): *m/z* = 2789.0 [M+3DCTB]$^+$, 2538.8 [M+2DCTB]$^+$, 2288.6 [M+DCTB]$^+$, 2038.5 [M]$^+$.

19b

Under an argon atmosphere, potassium carbonate (0.04 g, 0.27 mmol) was added to a solution of **18b** (0.10 g, 0.05 mmol) in THF (10 mL) and methanol (10 mL). The mixture was stirred at room temperature for 3 h and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:2) as eluent and yielded **19b** as a yellow solid (0.02 g, 24 %). Chemical formula: $C_{115}H_{144}N_4O_4Si_2$, M = 1702.57 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.12 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.44- 7.39 (m, 6H), 7.11-7.00 (m, 6H), 6.93 (s, 2H), 4.06-3.99 (m, 8H), 3.21 (s, 1H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 1.90-1.82 (m, 12H), 1.54-1.46 (m, 8H), 1.38-1.19 (m, 49H), 1.12-1.07 (m, 28H), 0.88-0.82 (m,16H). MS (MALDI-TOF, DCTB): *m/z* = 2201.3 [M+2DCTB]$^+$, 1951.2 [M+DCTB]$^+$, 1701.1 [M]$^+$.

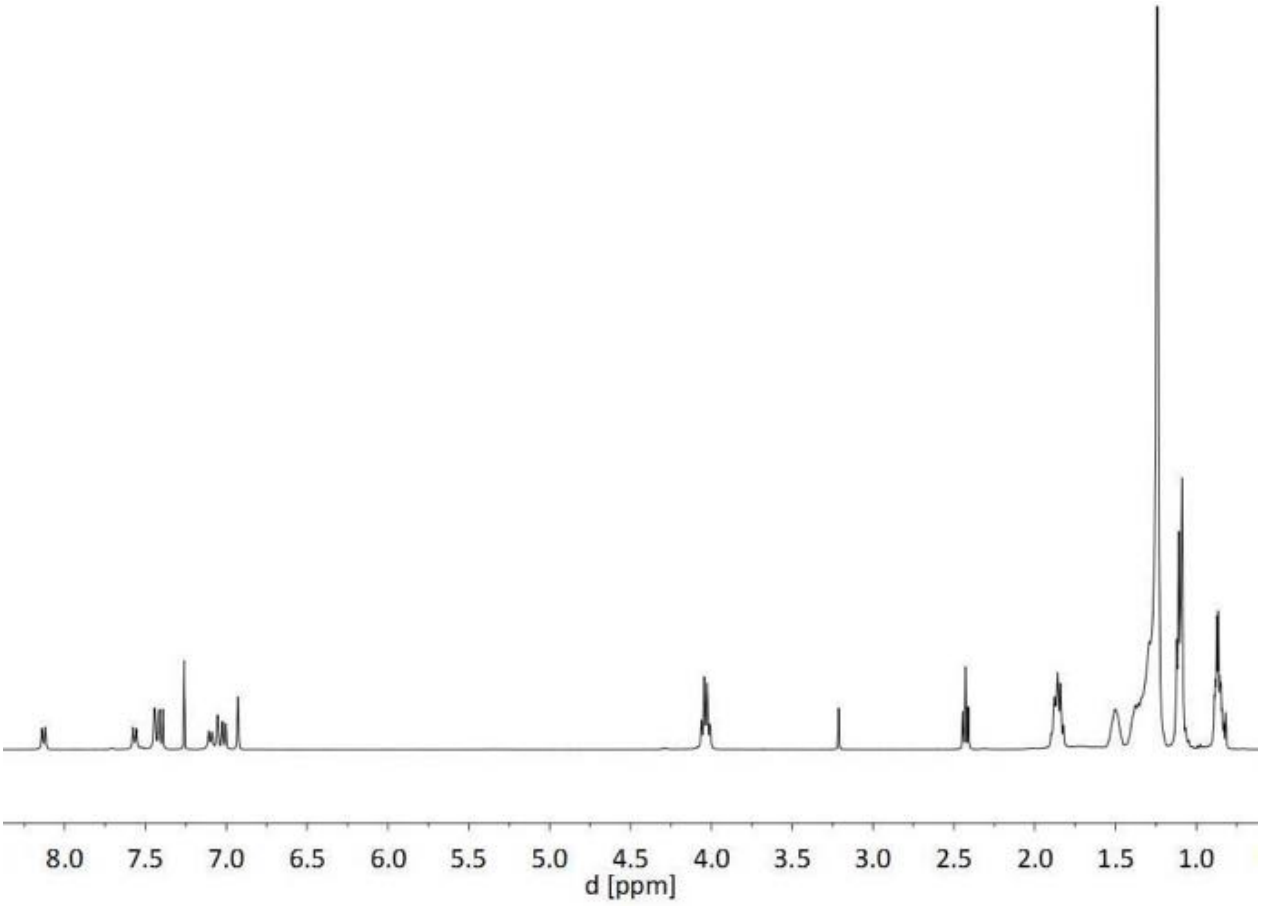


Figure S16. ^{1}H NMR of **19a**.

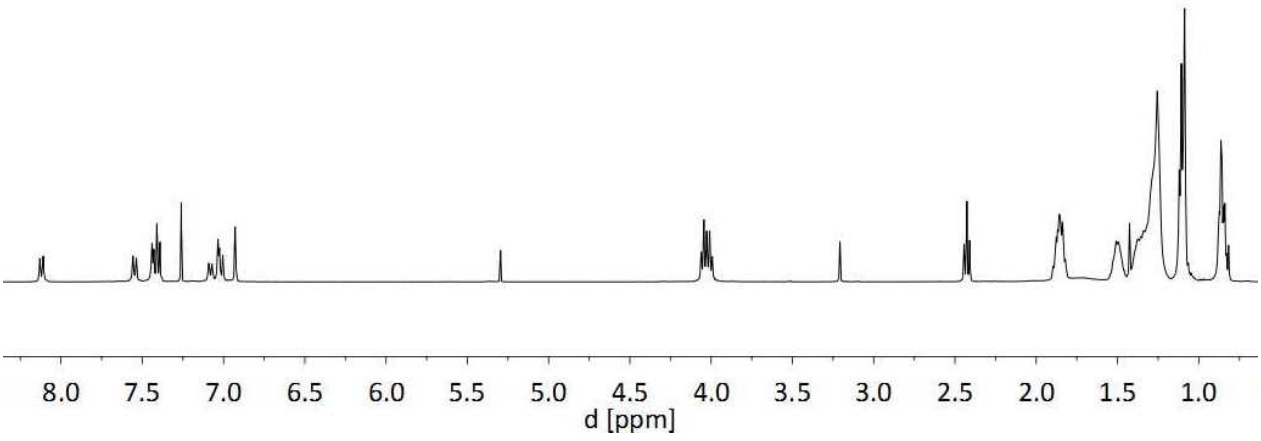
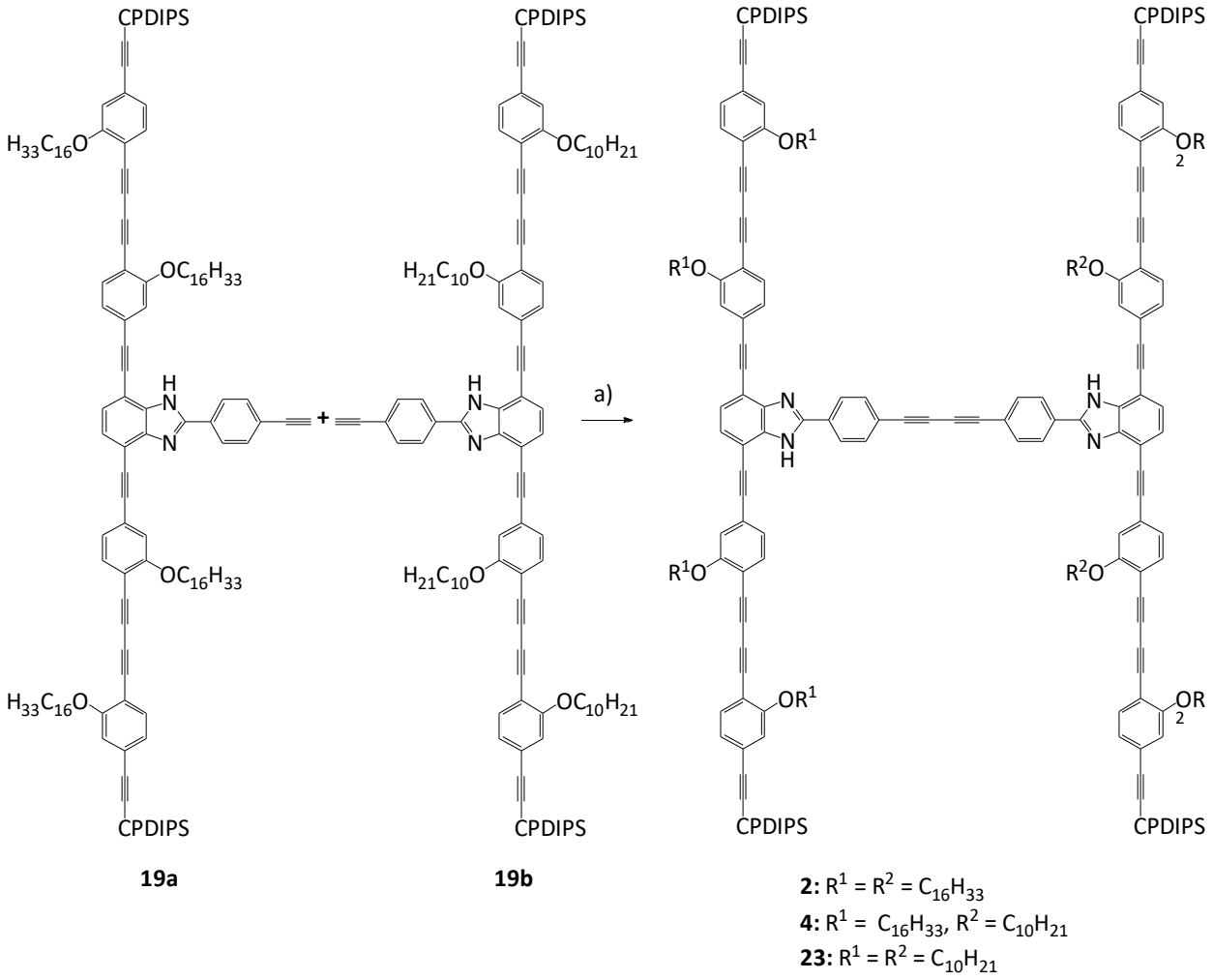


Figure S17. ^{1}H NMR of **19b**.

5.2.5 Synthesis of the H-shaped molecules 2, 4, 23

Scheme S9. Synthesis of **2**, **4**, **23**.



a) CuCl, TMEDA, O_2, CH_2Cl_2, 30 °C.

2, 4, 23

Under an argon atmosphere, copper(I) chloride (0.02 g, 0.2 mmol) and TMEDA (0.03 mL, 0.2 mmol) were added to a solution of **19a** (0.02 g, 0.01 mmol) and **19b** (0.02 g, 0.01 mmol) in dichloromethane (23 mL). With a small membrane pump, a steady flow of air was piped through the solution and the mixture was stirred at 30 °C for 2 h. After cooling down to room temperature the suspension was diluted with dichloromethane. The organic layer was separated and washed with water, 25 % NH_3, 10 % HCl and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:2) as eluent and yielded **2, 4, 23** as yellow solids (**2**: 7 mg, 31 %, **4**: 13 mg, 35 %, **23**: 2 mg, 13 %). **2** Chemical formula: $C_{278}H_{382}N_8O_8Si_4$, M = 4076.50 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.17 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.68 (d, $^3J_{HH}$ =

8.0 Hz, 4H), 7.48-7.46 (m, 8H), 7.40 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.18-7.12 (m, 8H), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 6.93 (s, 4H), 4.09-4.03 (m, 16H), 2.43 (t, $^3J_{HH}$ = 6.8 Hz, 8H), 1.92-1.83 (m, 24H), 1.62-1.57 (m, 16H), 1.57-1.48 (m, 16H), 1.39-1.18 (m, 178H), 1.12-1.09 (m, 56H), 0.89-0.82 (m, 32H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 134.2, 134.0, 133.1, 127.0, 124.6, 124.4, 124.0, 119.7, 115.0, 114.9, 112.5, 110.6, 110.2, 109.1, 107.4, 91.8, 69.0, 31.9, 29.7, 29.6, 29.6, 29.6, 29.6, 29.3, 29.0, 25.9, 22.7, 21.2, 20.8, 18.2, 17.9, 14.1, 11.7, 9.6. MS (MALDI-TOF, DCTB): *m/z* = 4327.3 [M+DCTB]$^+$, 4076.5 [M]$^+$. **4** Chemical formula: $C_{254}H_{334}N_8O_8Si_4$, M = 3739.85 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.17 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.65 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.46-7.45 (m, 8H), 7.40 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.16-7.10 (m, 8H), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 6.92 (s, 4H), 4.08-4.03 (m, 16H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 8H), 1.90-1.82 (m, 24H), 1.71-1.60 (m, 16H), 1.54-1.48 (m, 16H), 1.38-1.18 (m, 130H), 1.12-1.09 (m, 56H), 0.88-0.82 (m, 32H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 134.1, 134.1, 133.1, 127.0, 124.6, 124.4, 124.0, 119.7, 115.0, 114.9, 112.5, 107.4, 91.8, 69.0, 31.9, 29.7, 29.6, 29.6, 29.6, 29.6, 29.3, 29.0, 25.9, 22.7, 21.2, 20.8, 19.2, 17.9, 14.1, 11.7, 9.6. MS (MALDI-TOF, DCTB): *m/z* = 3990.3 [M+DCTB]$^+$, 3739.8 [M]$^+$. **23** Chemical formula: $C_{230}H_{286}N_8O_8Si_4$, M = 3403.21 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.17 (d, $^3J_{HH}$ = 6.8 Hz, 4H), 7.64 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.46- 7.44 (m, 8H), 7.40 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.15-7.10 (m, 8H), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 6.92 (s, 4H), 4.09-4.03 (m, 16H), 2.43 (t, $^3J_{HH}$ = 7.0 Hz, 8H), 1.89-1.83 (m, 24H), 1.65-1.56 (m, 16H), 1.54-1.48 (m, 16H), 1.38-1.18 (m, 82H), 1.15-1.05 (m, 53H), 0.88-0.82 (m, 32H). ^{13}C NMR (126 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.7, 160.6, 134.1, 133.1, 127.0, 124.6, 124.4, 124.0, 119.7, 115.0, 114.9, 112.5, 107.4, 91.8, 79.6, 79.2, 69.1, 69.1, 31.9, 29.6, 29.6, 29.6, 29.4, 29.4, 29.4, 29.3, 29.0, 29.0, 26.0, 25.9, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6. MS (MALDI-TOF, DCTB): *m/z* = 3653.8 [M+DCTB]$^+$, 3403.1 [M]$^+$.

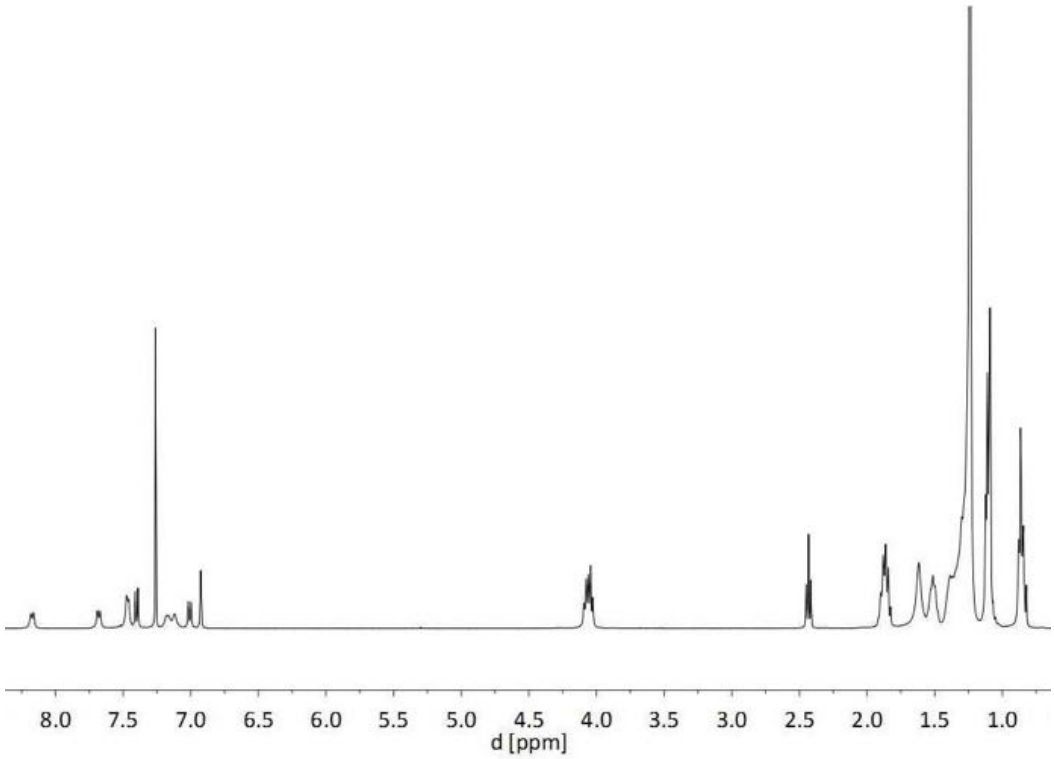


Figure S18. ^{1}H NMR of **2**.

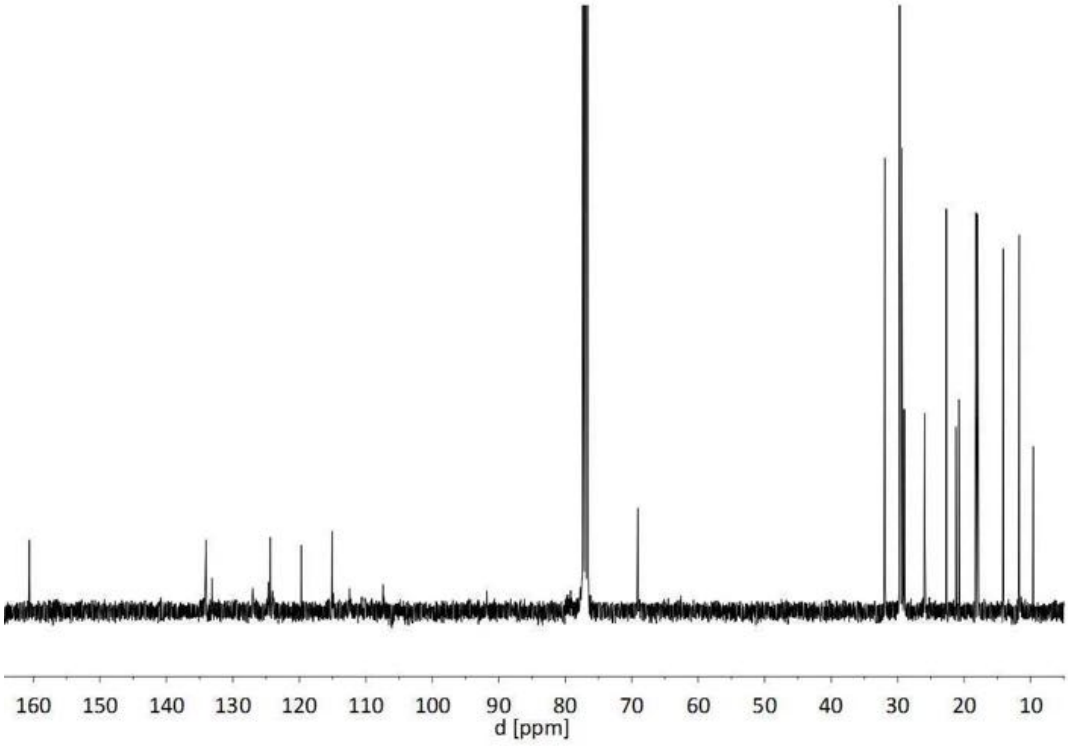


Figure S19. ^{13}C NMR of **2**.

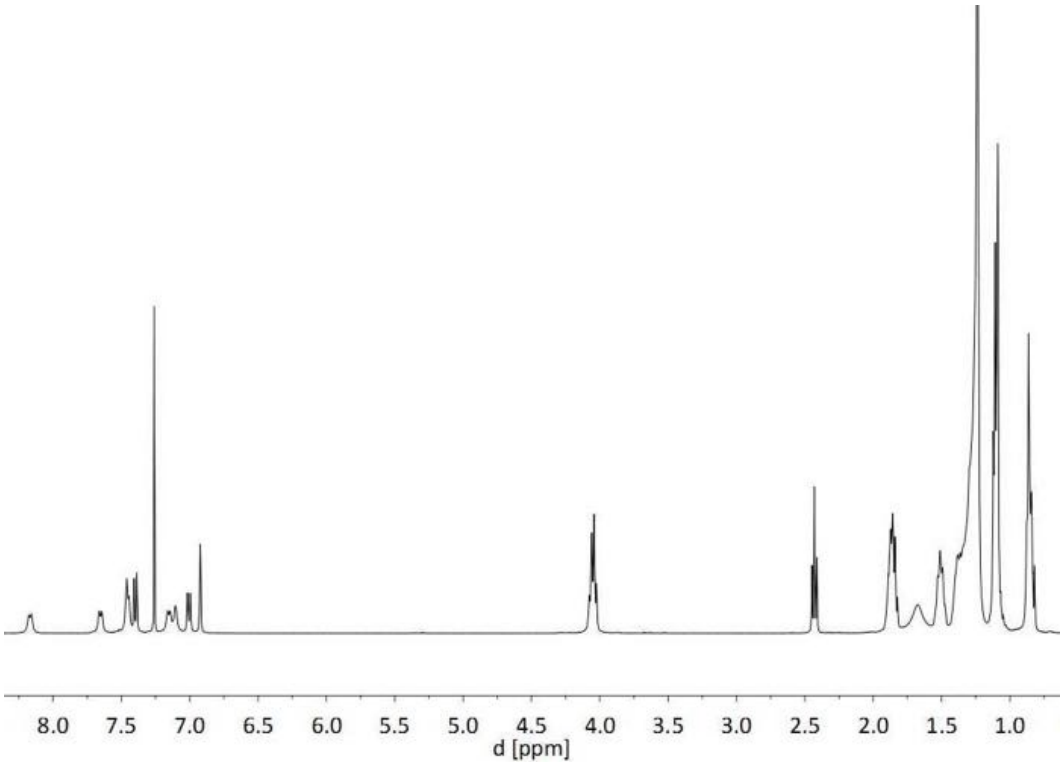


Figure S20. ^{1}H NMR of **4**.

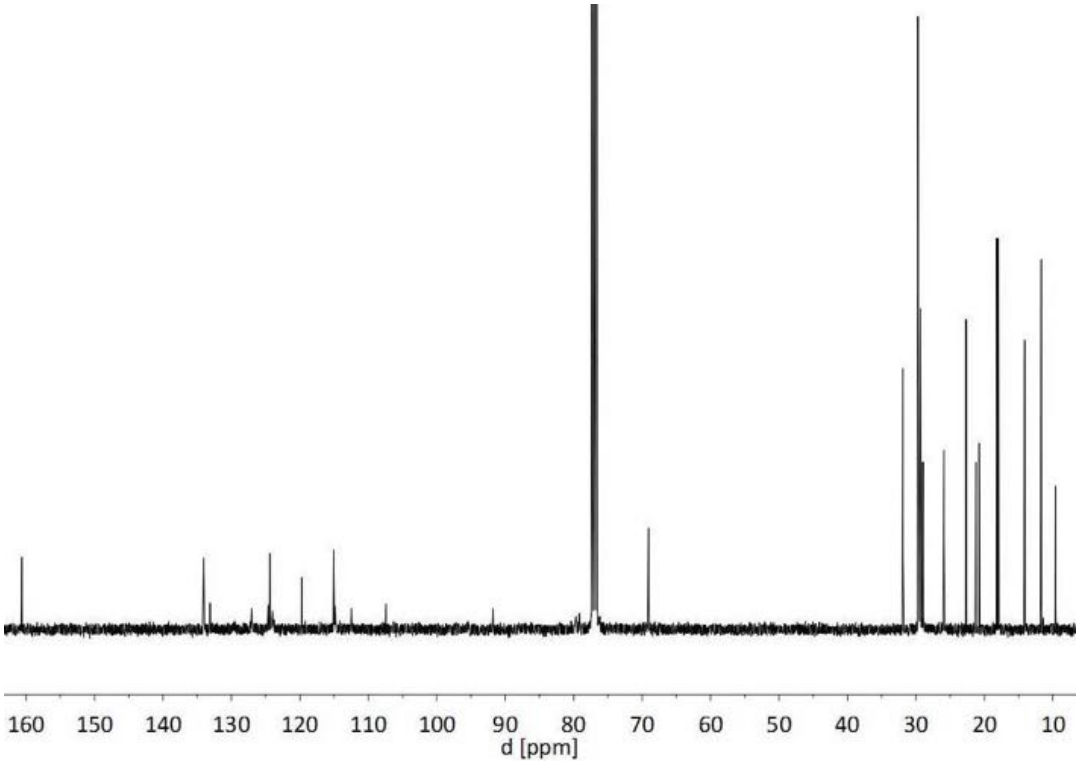


Figure S21. ^{13}C NMR of **4**.

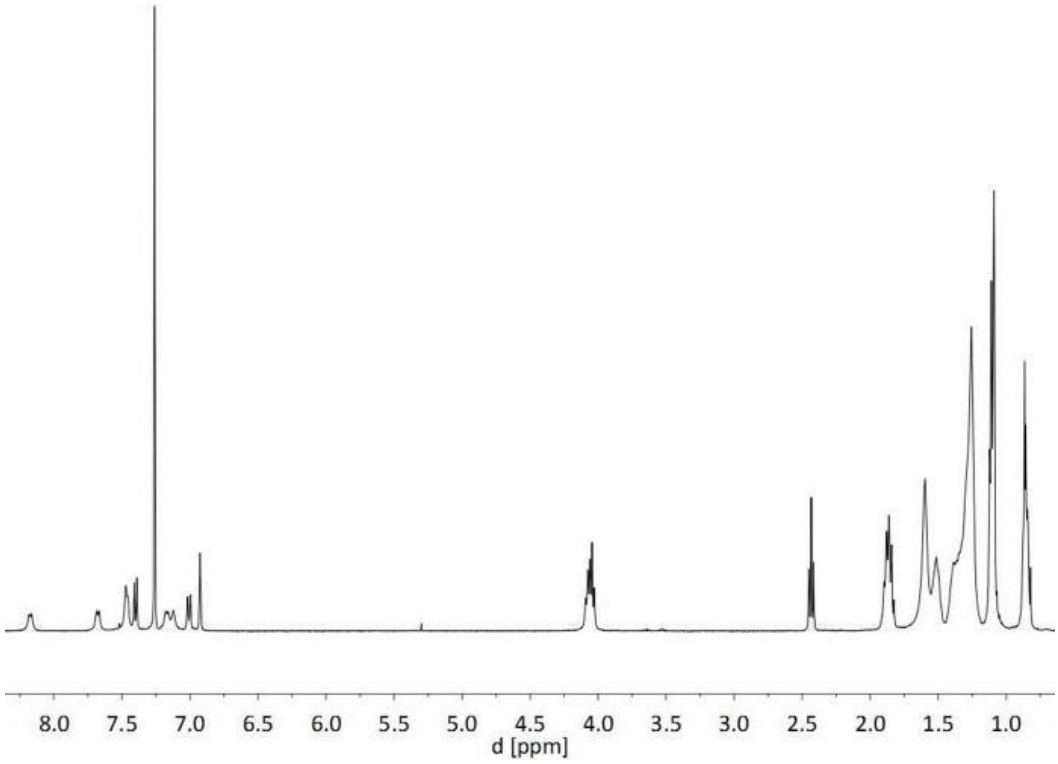


Figure S22. ^{1}H NMR of **23**.

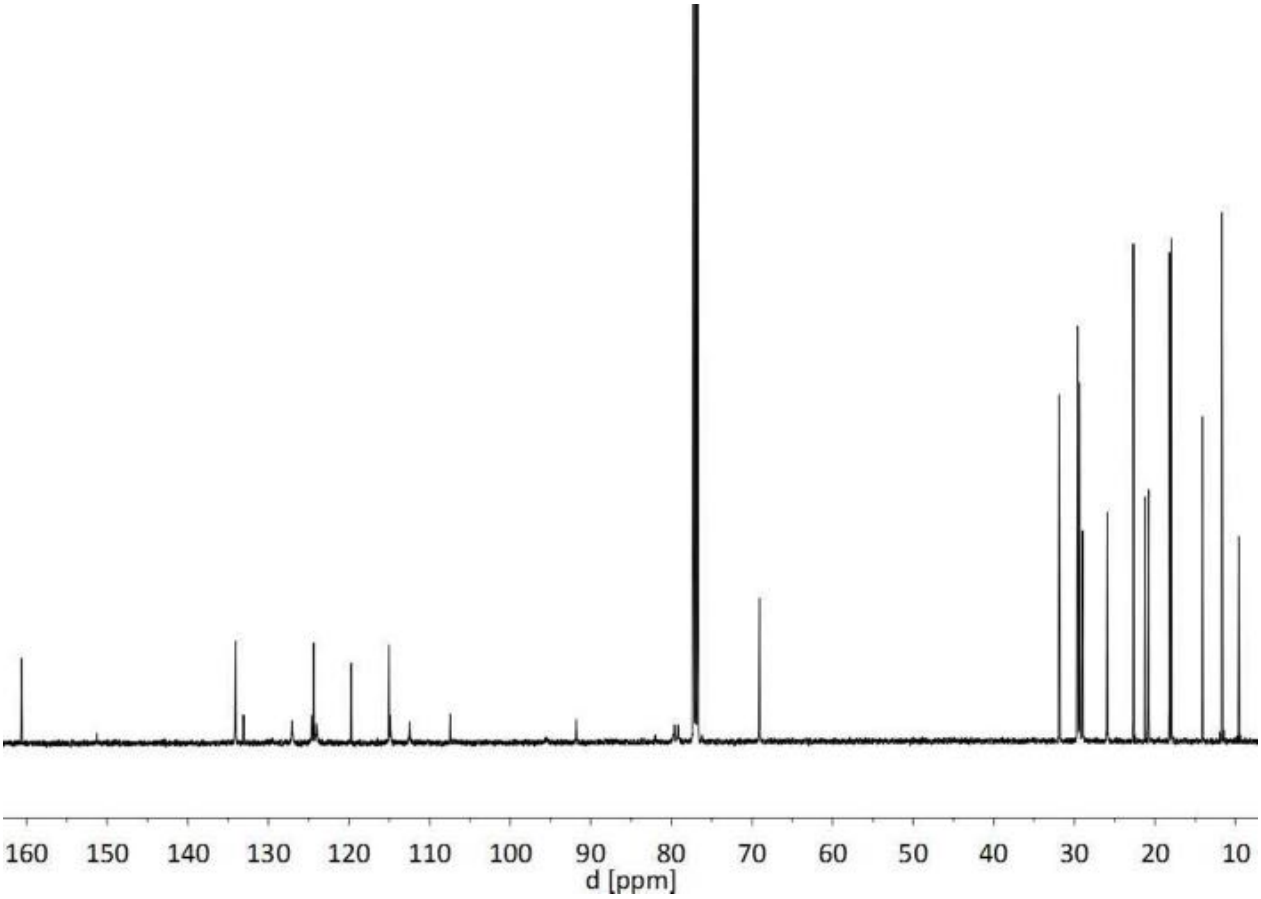


Figure S23. ^{13}C NMR of **23**.

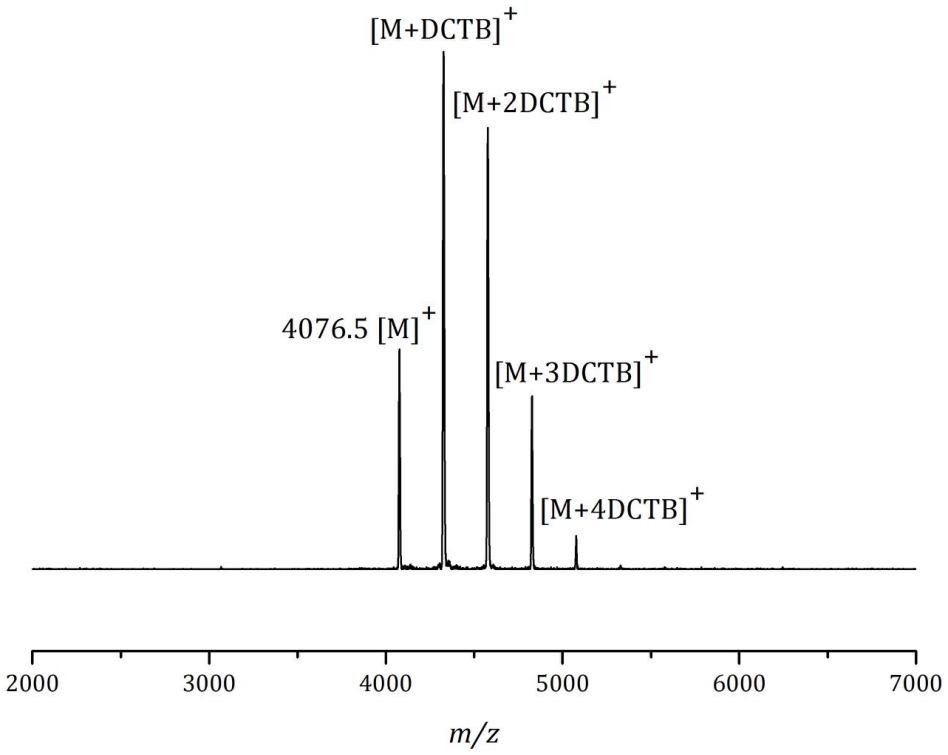


Figure S24. MALDI spectrum of **2** (matrix: DCTB).

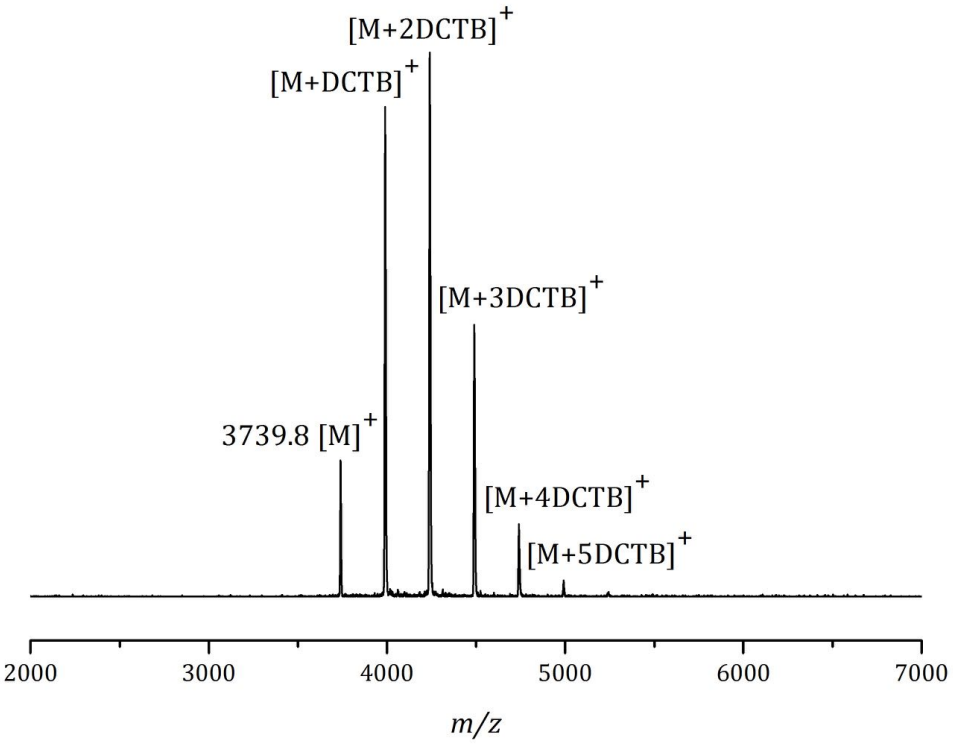


Figure S25. MALDI spectrum of **4** (matrix: DCTB).

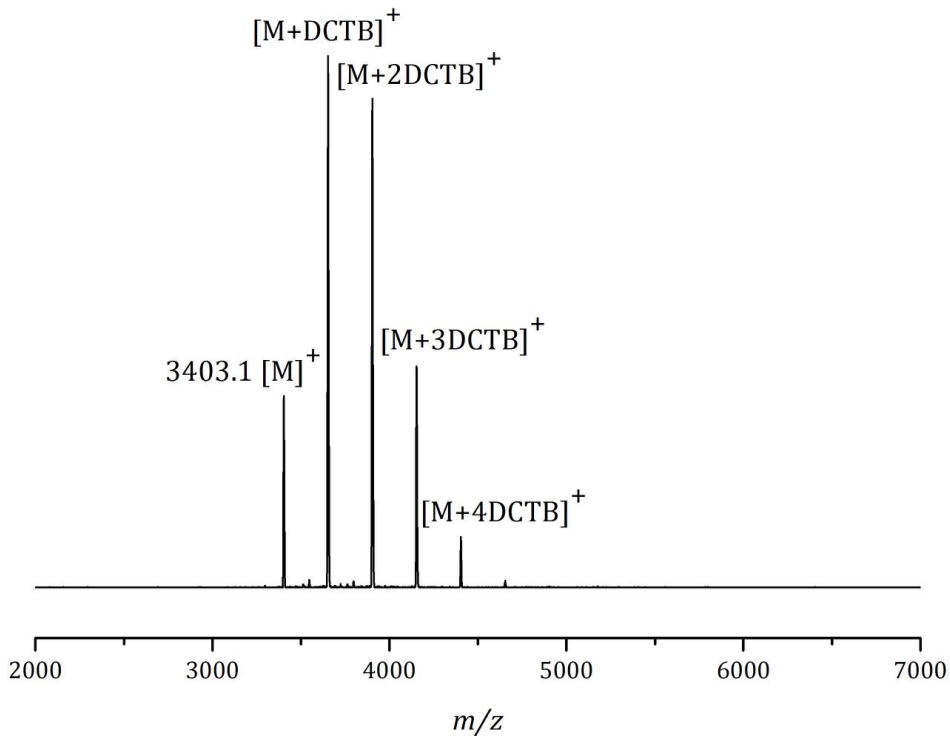


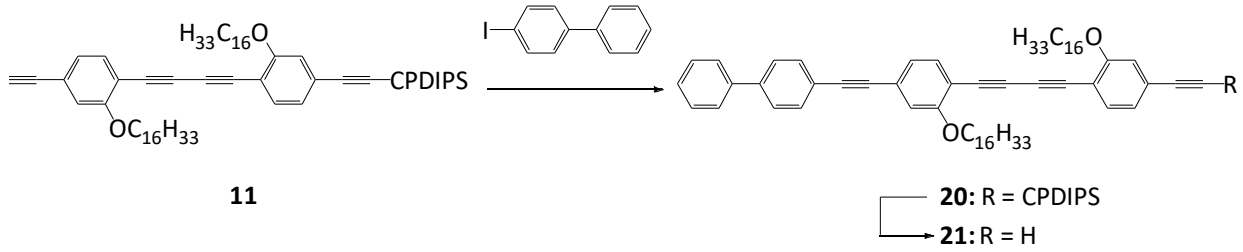
Figure S26. MALDI spectrum of **23** (matrix: DCTB).

5.3 Synthesis of 3

5.3.1 Synthetical strategy towards 3

Here we present the synthesis of a H-shaped molecule analogue to **2** but with biphenyl instead of CPDIPS end groups at the butadiynylene units. The butadiynylene building block with biphenyl end groups was prepared *via* palladium catalyzed *Sonogashira* coupling of **11** with 4-iodobiphenyl. Deprotection of **20** with TBAF gave the butadiynylene building block **21**, which was then used in another *Sonogashira* coupling with **12** to yield the T-shaped building block **22**. The H-shaped molecule **3** was obtained by CuCl catalyzed *Glaser* coupling with *in situ* deprotection of the TMS group with TBAF .

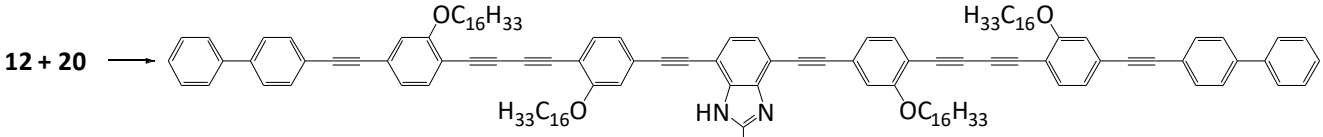
Scheme S10. Synthetical strategy towards **3**.



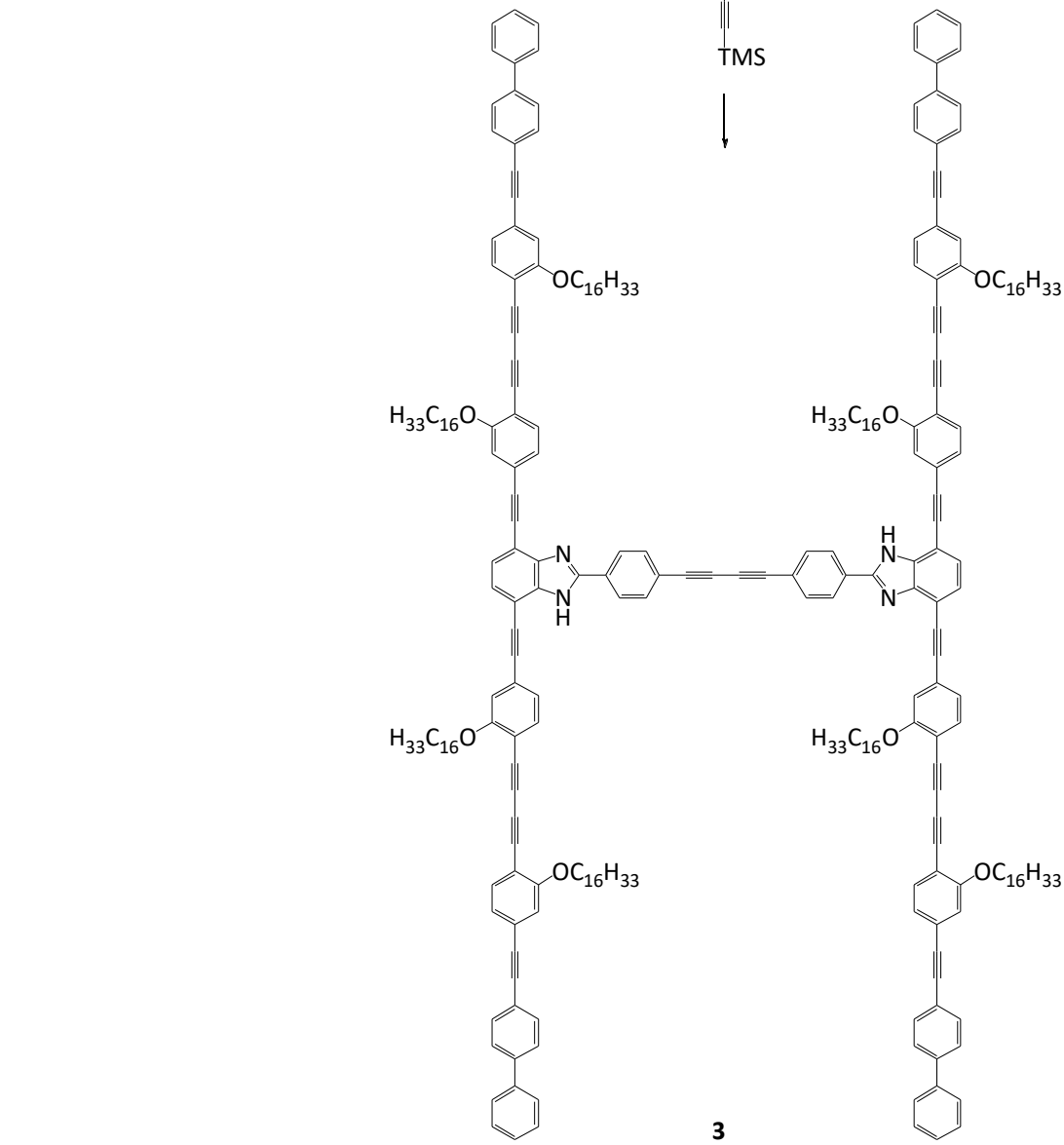
11

20: R = CPDIPS

21: R = H



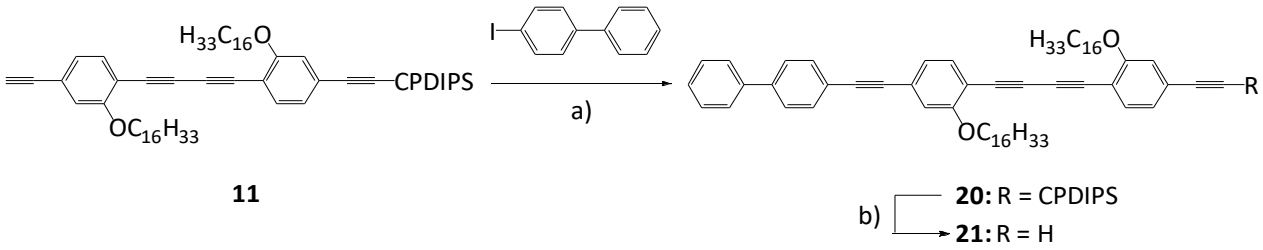
22



3

5.3.2 Synthesis of the butadiynylene building block 21

Scheme S11. Synthesis of **21**.



a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, piperidine, 40 °C; b) TBAF, THF, r. t.

20

Under an argon atmosphere, 4-iodobiphenyl (0.08 g, 0.27 mmol) was added to a solution of **11** (0.30 g, 0.33 mmol), $PdCl_2(PPh_3)_2$ (0.008 g, 0.01 mmol), triphenylphosphane (0.008 g, 0.03 mmol) and copper(I) iodide (0.004 g, 0.02 mmol) in piperidine (30 mL). The mixture was stirred at 40 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (2:1) as eluent and yielded **20** as a yellow solid (0.27 g, 93 %). Chemical formula: $C_{74}H_{101}NO_2Si$, M = 1064.71 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.63-7.60 (m, 6H), 7.48-7.35 (m, 5H), 7.08 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 7.03 (d, $^4J_{HH}$ = 1.0 Hz, 1H), 7.01 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 6.93 (d, $^4J_{HH}$ = 1.0 Hz, 1H), 4.09-4.03 (m, 4H), 2.44 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 1.91-1.83 (m, 6H), 1.59-1.48 (m, 4H), 1.40-1.20 (m, 48H), 1.13-1.07 (m, 14H), 0.90-0.83 (m, 8H). ^{13}C NMR (101 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.6, 141.3, 140.2, 134.2, 134.0, 132.1, 128.9, 127.7, 127.1, 127.0, 125.1, 124.6, 124.4, 123.8, 121.7, 119.7, 115.1, 114.7, 112.6, 112.0, 107.4, 79.7, 79.4, 79.3, 79.0, 69.1, 69.0, 31.9, 29.7, 29.7, 29.7, 29.6, 29.4, 29.0, 29.0, 25.9, 25.9, 22.7, 21.2, 20.8, 18.2, 18.0, 14.1, 11.7, 9.6. MS (MALDI-TOF, DCTB): *m/z* = 1313.0 $[M+DCTB]^+$, 1063.8 $[M]^+$, 852.6 $[M-C_{15}H_{29}]^+$.

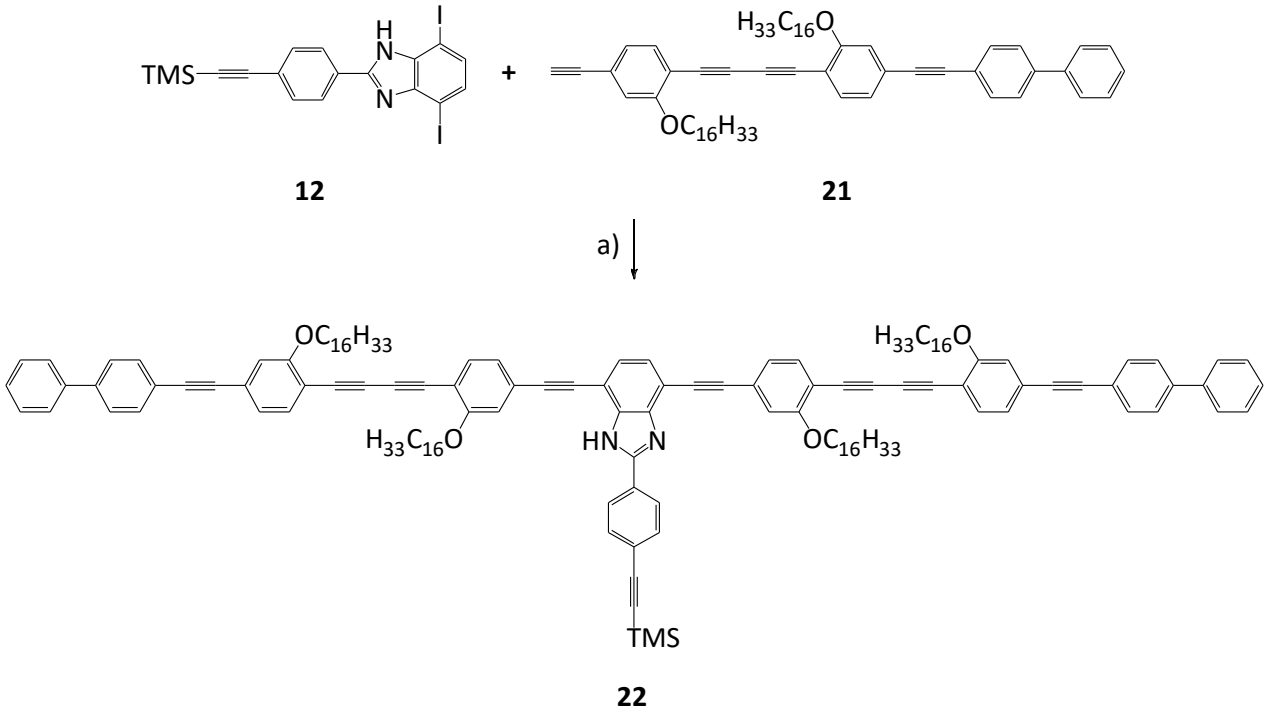
21

Under an argon atmosphere, TBAF (1M in THF, 0.5 mL, 0.50 mmol) was added to a solution of **20** (0.27 g, 0.25 mmol) in THF (20 mL). The mixture was stirred at room temperature for 3 h, quenched by addition of water and then diluted with dichloromethane. The organic layer was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using

cyclohexane – dichloromethane (4:1) as eluent and yielded **21** as a yellow solid (0.20 g, 87 %). Chemical formula: $C_{64}H_{82}O_2$, M = 883.36 g/mol. ^{1}H NMR (500 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 7.63-7.61 (m, 6H), 7.48-7.36 (m, 5H), 7.09 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 7.06-7.03 (m, 2H), 6.98 (d, $^4J_{HH}$ = 1.0 Hz, 1H), 4.07 (t, $^3J_{HH}$ = 6.8 Hz, 2H), 4.03 (t, $^3J_{HH}$ = 6.5 Hz, 2H), 3.19 (s, 1H), 1.91-1.84 (m, 4H), 1.56-1.43 (m, 4H), 1.35-1.19 (m, 48H), 0.92-0.88 (m, 6H). ^{13}C NMR (126 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.7, 160.5, 141.3, 140.2, 134.1, 134.1, 132.1, 128.8, 127.7, 127.0, 127.0, 125.1, 124.2, 123.8, 123.8, 121.7, 115.3, 114.7, 112.7, 111.9, 91.5, 89.9, 83.3, 79.7, 79.4, 79.2, 79.1, 78.8, 69.0, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.0, 28.9, 25.9, 25.9, 22.7, 14.1. MS (MALDI-TOF, DCTB): *m/z* = 1132.9 $[M+DCTB]^+$, 882.7 $[M]^+$.

5.3.3 Synthesis of the T-shaped building block 22

Scheme S12. Synthesis of **22**.



a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, piperidine, 40 °C.

22

Under an argon atmosphere, **21** (0.19 g, 0.22 mmol) was added to a solution of **12** (0.05 g, 0.10 mmol), $PdCl_2(PPh_3)_2$ (0.01 g, 0.01 mmol), triphenylphosphane (0.01 g, 0.04 mmol) and copper(I) iodide (0.004 g, 0.02 mmol) in piperidine (20 mL). The mixture was stirred at 40 °C overnight, cooled down to room temperature and then diluted with dichloromethane. The organic layer was separated and washed with water, 10 % AcOH, 2M NaOH (aq) and brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using cyclohexane – dichloromethane (1:1) as eluent and yielded **22** as a yellow solid (0.14 g, 70 %) Chemical formula: $C_{146}H_{178}N_2O_4Si$, M = 2053.13 g/mol. ^{1}H NMR (400 MHz, C*D*Cl_3,r.t.): δ [ppm] = 8.14 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.62-7.58 (m, 8H), 7.54-7.48 (m, 8H), 7.45-7.34 (m, 10H), 7.11 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.04 (s, 2H), 6.93-6.88 (m, 4H), 4.08 (t, $^3J_{HH}$ = 6.8 Hz, 4H), 3.96 (t, $^3J_{HH}$ = 6.0 Hz, 4H), 1.92-1.82 (m, 8H), 1.55-1.46 (m, 8H), 1.39-1.19 (m, 97H), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 12H), 0.27 (s, 9H). ^{13}C NMR (101 MHz, C*D*Cl_3,r.t.): δ [ppm] = 160.6, 160.4, 151.8, 141.1, 140.2, 134.3, 134.0, 132.5, 132.1, 128.8, 127.7, 127.0, 127.0, 126.7, 125.4, 125.1, 124.0, 121.7, 114.6, 114.5, 111.9, 104.2, 97.2, 91.4, 90.0, 69.0, 31.9, 29.8, 29.7, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1, 29.0, 26.0, 25.9, 22.7, 14.1,

-0.2. MS (MALDI-TOF, DCTB): *m/z* = 2551.5 $[M+2\ DCTB]^+$, 2301.4 $[M+DCTB]^+$, 2051.3 $[M]^+$.

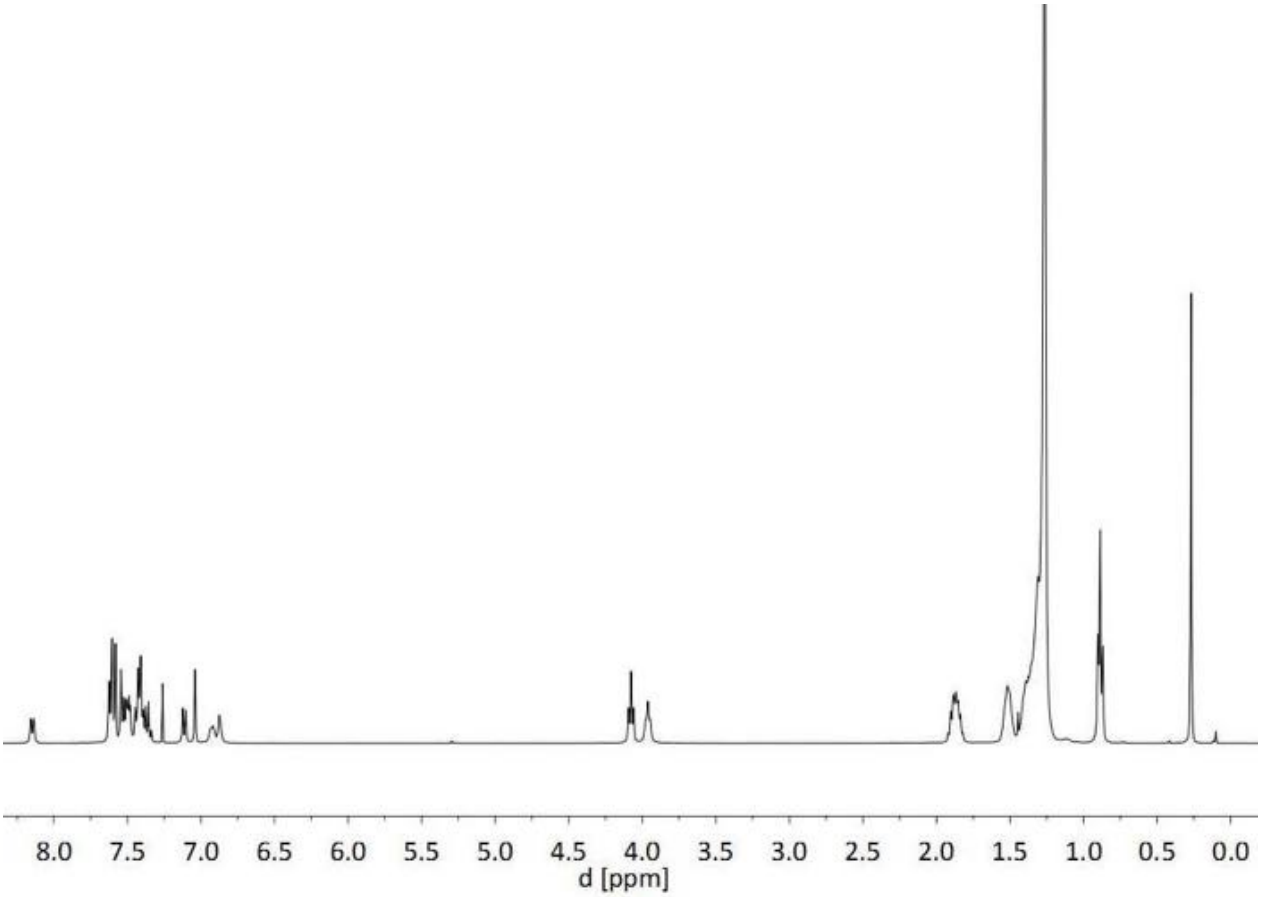


Figure S27. ^{1}H NMR of **22**.

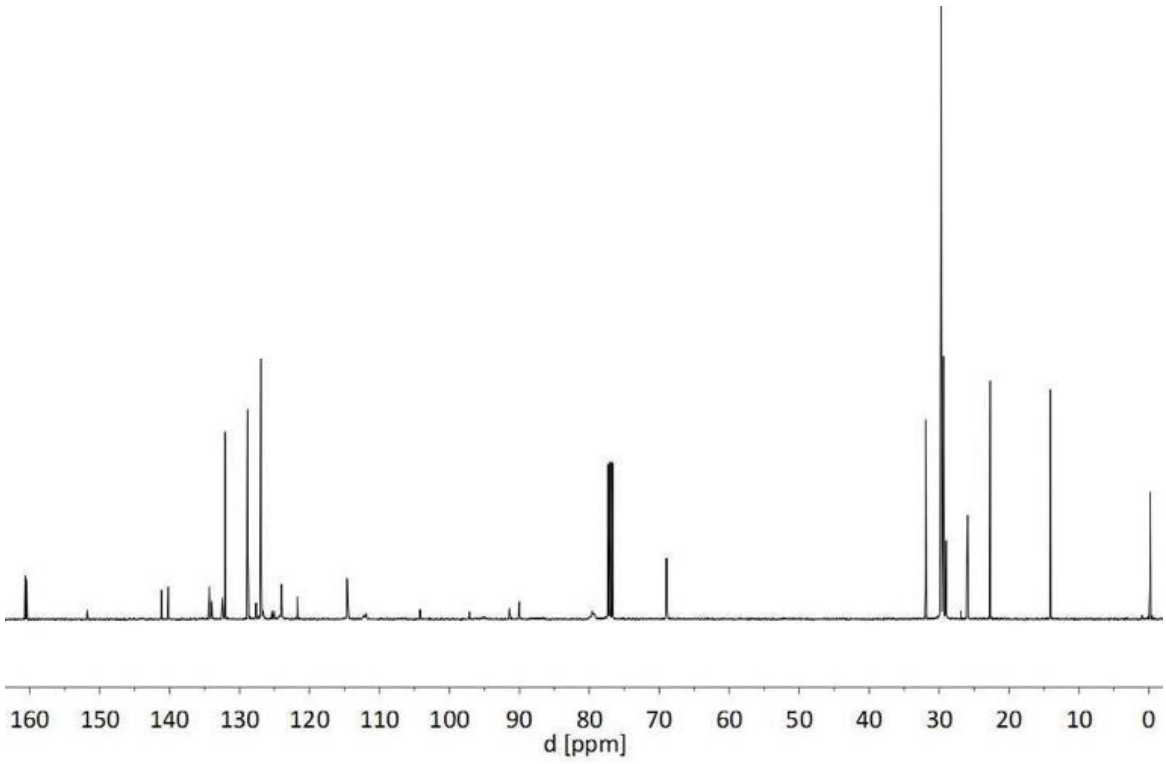
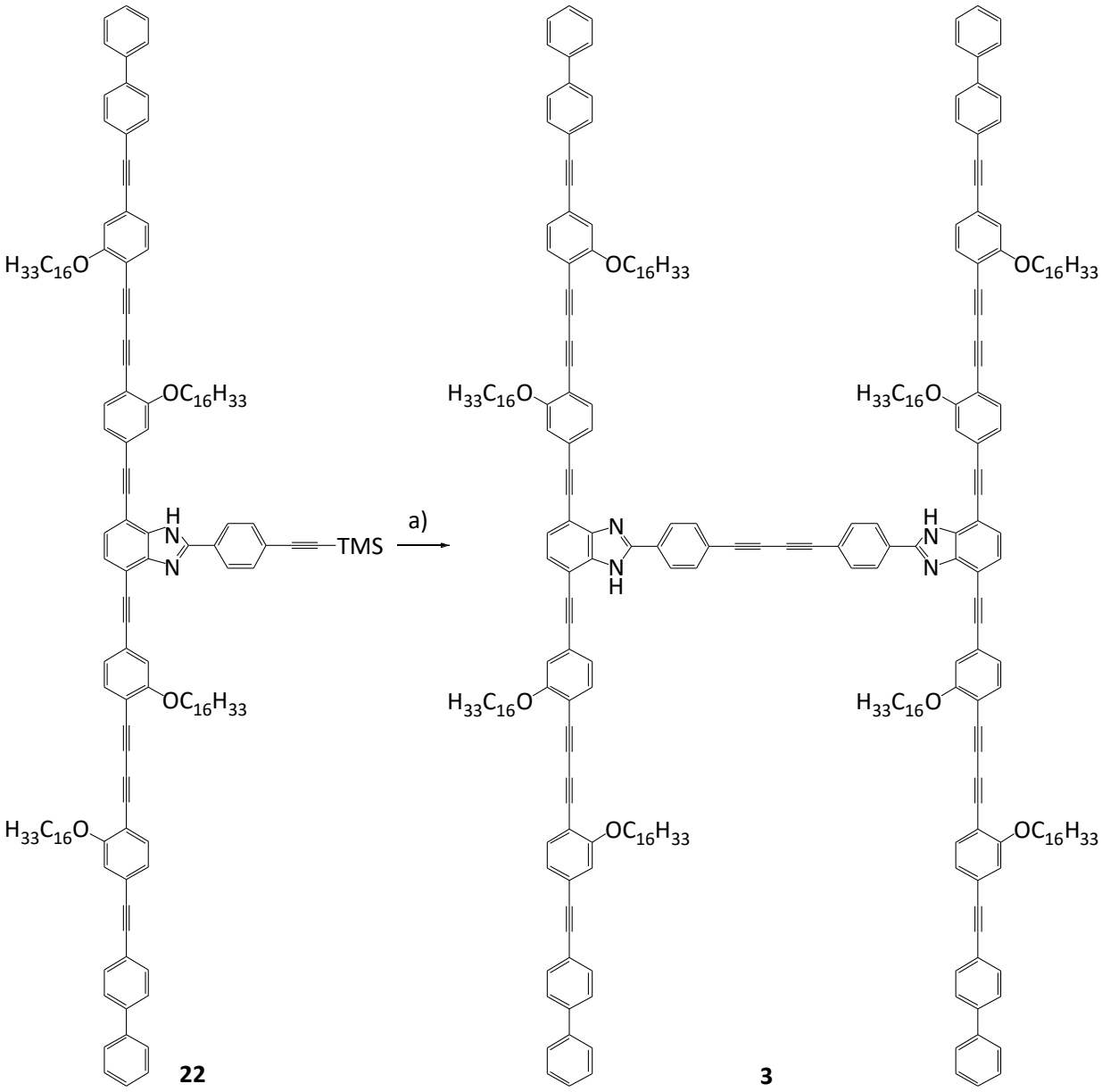


Figure S28. ^{13}C NMR of **22**.

5.3.4 Synthesis of the H-shaped molecule 3

Scheme S13. Synthesis of **3**.



a) CuCl, TMEDA, O_2, TBAF, THF, 40 °C.

3

Under an argon atmosphere, copper(I) chloride (0.06 g, 0.66 mmol), TMEDA (0.1 mL, 0.66 mmol) and TBAF (1M in THF, 0.1 mL, 0.1 mmol) were added to a solution of **22** (0.07 g, 0.03 mmol) in THF (30 mL). With a small membrane pump, a steady flow of air was piped through the solution and the mixture was stirred at 40 °C overnight. After cooling down to room temperature the suspension was diluted with dichloromethane. The organic layer was separated and washed with water, 25 % NH_3, 10 % HCl and brine, dried over $MgSO_4$ and the

solvent was evaporated. The crude product was purified by *rec*-GPC and yielded **3** as a yellow solid (0.05 g, 73 %). Chemical formula: $C_{286}H_{338}N_4O_8$, M = 3959.87 g/mol. ^{1}H NMR (400 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 8.17 (d, $^3J_{HH}$ = 7.2 Hz, 4H), 7.61-7.54 (m, 32H), 7.47-7.42 (m, 16H), 7.37-7.33 (m, 4H), 7.10-6.99 (m, 16H), 4.08-4.02 (m, 16H), 1.92-1.82 (m, 16H), 1.57-1.46 (m, 16H), 1.39-1.15 (m, 194H), 0.89-0.84 (m, 24H). ^{13}C NMR (126 MHz, C*D*Cl$_3$,r.t.): δ [ppm] = 160.6, 160.6, 141.2, 140.2, 139.8, 134.3, 134.1, 133.1, 128.9, 127.7, 127.0, 127.0, 123.9, 121.8, 114.7, 91.4, 90.0, 69.0, 31.9, 29.8, 29.7, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 29.4, 29.1, 29.0, 26.0, 25.9, 22.7, 14.1. MS (MALDI-TOF, dithranol): *m/z* = 4410.5 [M+2dithranol]$^+$, 4185.1 [M+dithranol]$^+$, 3959.6 [M]$^+$.

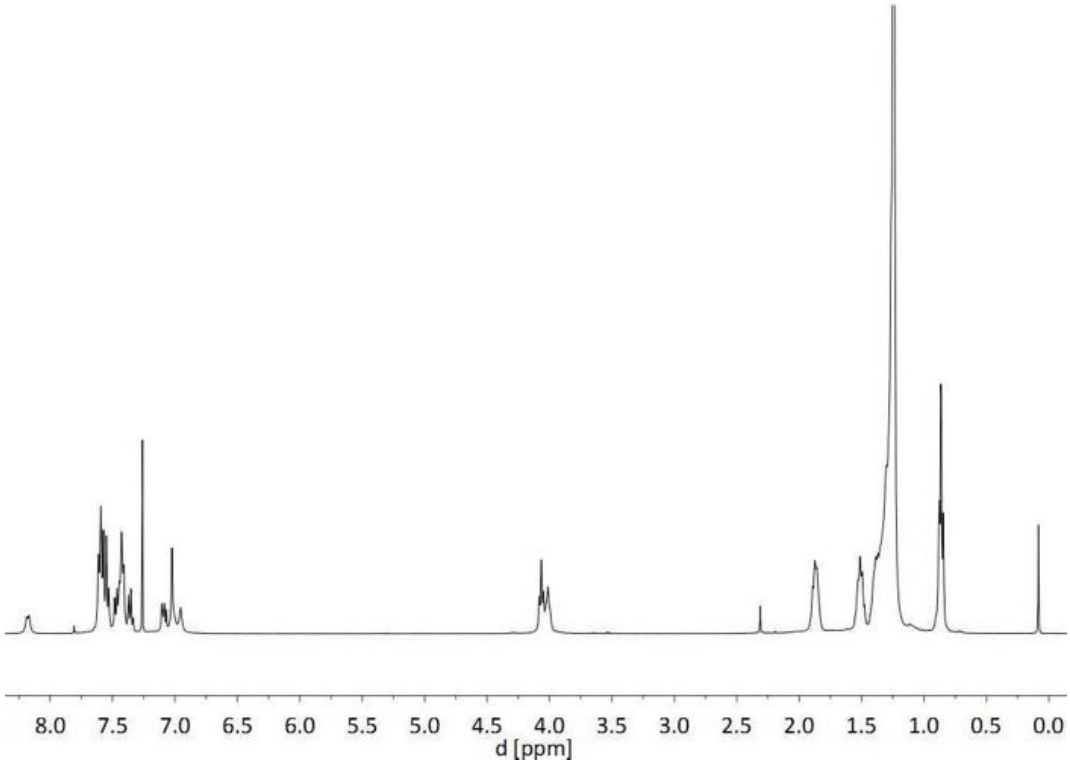


Figure S29. ^{1}H NMR of **3**.

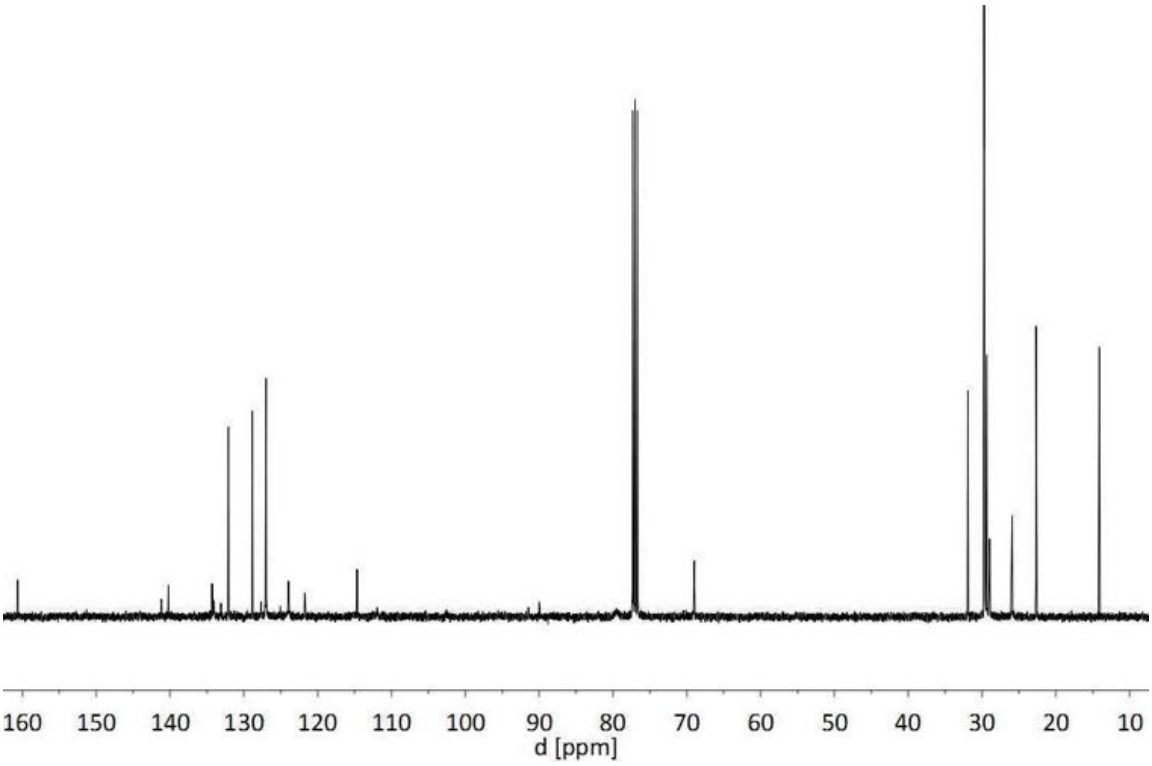


Figure S30. ^{13}C NMR of **3**.

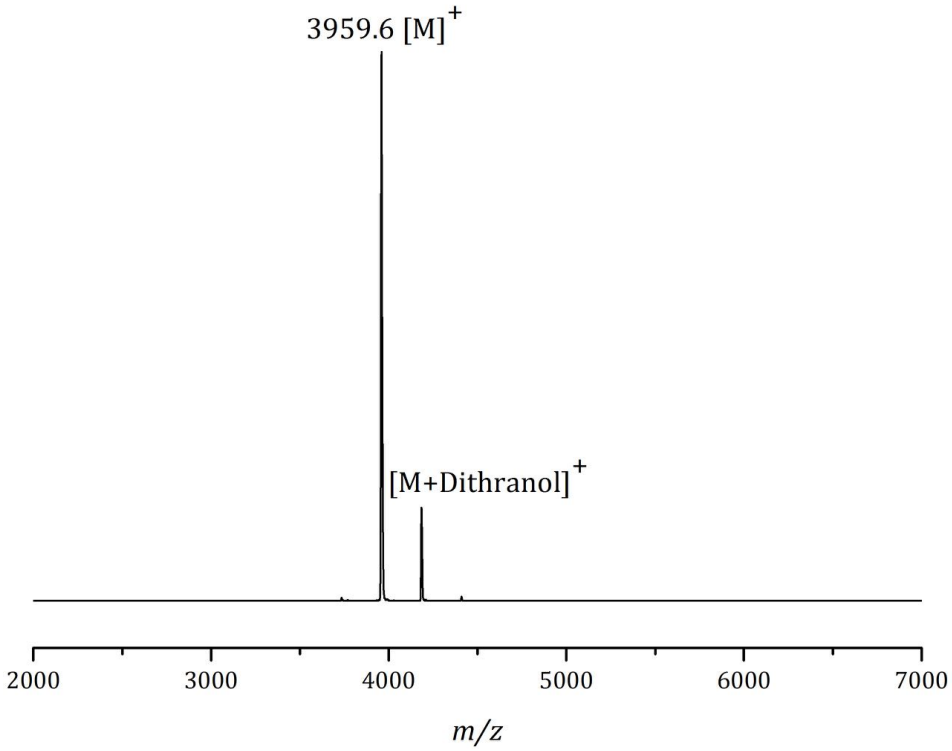


Figure S31. MALDI MS of **3** (matrix: dithranol).

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