Supporting Information

Sequence-defined Macrocycles for Understanding and Controlling the Build-up of Hierarchical Order in Self-assembled 2D Arrays

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S1. General Experimental Procedures

Reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160-200 mesh, Sorbent Technologies, USA). Thin-layer chromatography (TLC) was performed on pre-coated silica gel plates (0.25 mm thick, #1615126, Sorbent Technologies, USA) and observed under UV light. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Inova (600 MHz, 500 MHz, and 400 MHz) and Varian VXR (400 MHz) spectrometers at room temperature (298 K). Chemical shifts were referenced to residual solvent peaks. High-resolution electrospray ionization and electron ionization mass spectrometry (HR-ESI-MS and HR-EI-MS) was performed on a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer.

STM experiments were carried out on an Agilent Technologies 5500 PicoPlus STM using a Picoscan 1.18.1 controller in constant-current mode. Tips were mechanically cut from Pt/Ir wire (80:20, 0.25 mm diameter). Voltage pulses between 2 to 10 V with 1 to 3 ms durations were occasionally applied to improve image quality. Unless noted, all experiments were conducted at room temperature. Samples were prepared by dropping 3 μL of solution using a micropipette onto a freshly cleaved HOPG (highly oriented pyrolytic graphite) surface (ZYB, 10 × 10 × 1 mm). HOPG was mechanically cleaved using scotch tape, and a minor circular impression was made in the HOPG surface by pressing a viton o-ring on the surface for several seconds. The impression prevented the liquid sample from wicking off the HOPG surface. Solutions were prepared with 1,2,4-trichlorobenzene (≥ 99%). Typical scanning parameters ranged from I_t = 0.03 to 0.4 nA, V_{sample} = −0.3 to −1.2 V. High-resolution STM images were corrected for drift effects and piezo scanner calibration by comparison to lattice measurements of the underlying HOPG, which were recorded by using scan conditions different from those used to measure molecular assemblies: I_t = 0.1 to 0.3 nA, V_{sample} = −0.002 to −0.005 V (referred to as "HOPG corrected"). Unit-cell measurements (including angles relative to the HOPG lattice) were acquired after correcting the high-resolution images and averaging the distances.

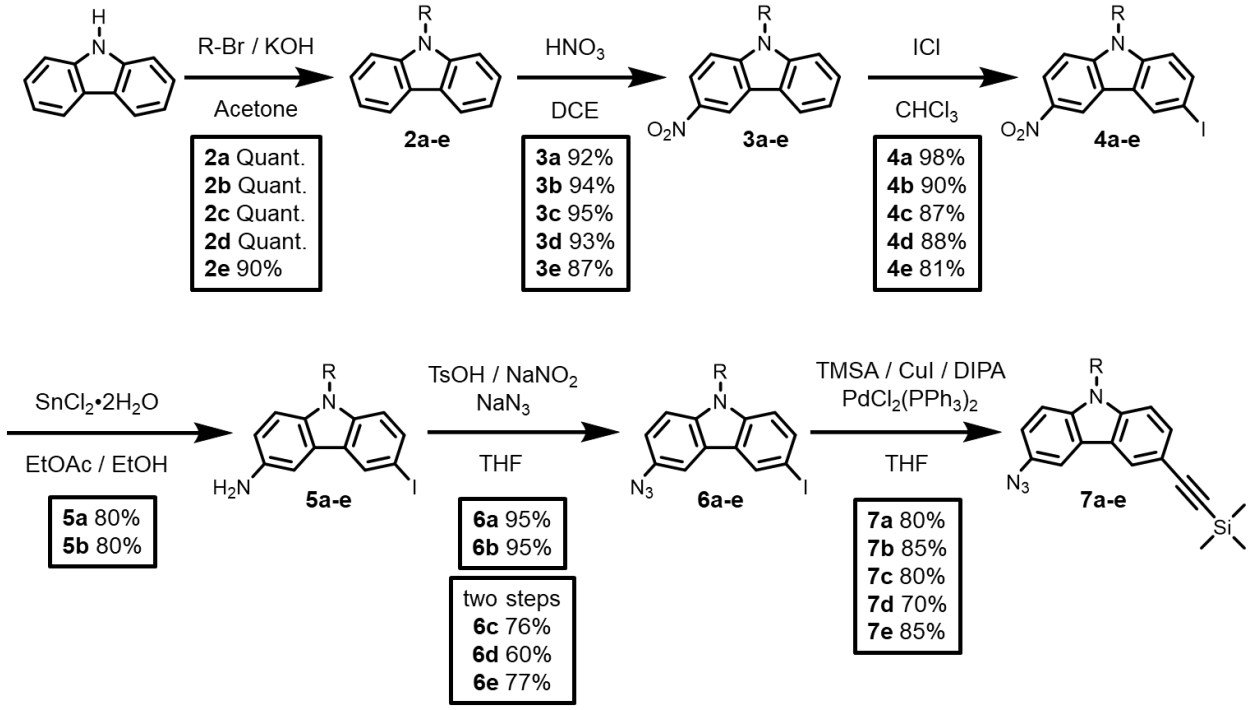
S2. Table of Synthesized and Characterized compounds

Shorthand Name	Compound Number	New/Known	^{1}H NMR	^{13}C NMR	HRMS
C_6 carbazole	**2a**	Known	X		
C_{10} carbazole	**2b**	Known	X		
C_{18} carbazole	**2c**	New	X	X	X
MeCy carbazole	**2d**	New	X	X	X
HEG carbazole	**2e**	New	X	X	X
C_6 carbazole - NO_2	**3a**	Known	X		
C_{10} carbazole - NO_2	**3b**	Known	X		
C_{18} carbazole - NO_2	**3c**	New	X	X	X
MeCy carbazole - NO_2	**3d**	New	X	X	X
HEG carbazole - NO_2	**3e**	New	X	X	X
C_6 carbazole - NO_2 / I	**4a**	Known	X		
C_{10} carbazole - NO_2 / I	**4b**	Known	X		
C_{18} carbazole - NO_2 / I	**4c**	New	X	X	X
MeCy carbazole - NO_2 / I	**4d**	New	X	X	X
HEG carbazole - NO_2 / I	**4e**	New	X	X	X
C_6 carbazole - NH_2 / I	**5a**	New	X	X	X
C_{10} carbazole - NH_2 / I	**5b**	New	X	X	X
C_6 carbazole - N_3 / I	**6a**	Known	X		
C_{10} carbazole - N_3 / I	**6b**	Known	X		
C_{18} carbazole - N_3 / I	**6c**	New	X	X	X
MeCy carbazole - N_3 / I	**6d**	New	X	X	X
HEG carbazole - N_3 / I	**6e**	New	X	X	X
C_6 carbazole - N_3 / TMS	**7a-TMS**	New	X	X	X
C_{10} carbazole - N_3 / TMS	**7b-TMS**	New	X	X	X
C_{18} carbazole - N_3 / TMS	**7c-TMS**	New	X	X	X
MeCy carbazole - N_3 / TMS	**7d-TMS**	New	X	X	X
HEG carbazole - N_3 / TMS	**7e-TMS**	New	X	X	X
C_6 carbazole - N_3 / Alk	**7a**	Known	X		
C_{10} carbazole - N_3 / Alk	**7b**	Known	X		
C_{18} carbazole - N_3 / Alk	**7c**	New	X	X	X
C_6 carbazole - NH_2 / Alk	**8a**	New	X	X	X
C_{10} carbazole - NH_2 / Alk	**8b**	New	X	X	X
C_6 C_6 dimer - NH_2 / Alk	**dimer-66**	New	X	X	X
C_{10} C_{10} dimer - NH_2 / Alk	**dimer-1010**	New	X	X	X
C_6 MeCy dimer - NH_2 / Alk	**dimer-6MeCy**	New	X	X	X
C_{10} C_{10} C_{10} trimer - NH_2 / TMS	**101010-NH2-TMS**	New	X	X	X
C_6 C_6 C_{18} trimer - NH_2 / TMS	**6618-NH2-TMS**	New	X	X	X

Shorthand Name	Compound Number	New/Known	^{1}H NMR	^{13}C NMR	HRMS
C_6 C_6 HEG trimer - NH_2 / TMS	**66HEG-NH2-TMS**	New	X	X	X
C_6 MeCy C_{10} trimer - NH_2 / TMS	**6MeCy10-NH2-TMS**	New	X	X	X
C_{10} C_{10} C_{10} trimer - N_3 / Alk	**trimer-101010**	New	X	X	X
C_6 C_6 C_{18} trimer - N_3 / Alk	**trimer-6618**	New	X	X	X
C_6 C_6 HEG trimer - N_3 / Alk	**trimer-66HEG**	New	X	X	X
C_6 MeCy C_{10} trimer - N_3 / Alk	**trimer-6MeCy10**	New	X	X	X
Hexyl Tricarb	**TC-6**	New	X	X	X
Decyl Tricarb	**TC-10**	New	X	X	X
Octadecyl Tricarb	**TC-18**	New	X	X	X
Dihexyl Octadecyl Tricarb	**TC6618**	New	X	X	X
Dihexyl HEG Tricarb	**TC-66HEG**	New	X	X	X
Hexyl MeCy Decyl Tricarb	**TC-610MeCy**	New	X	X	X

S3. General Synthesis of Building Blocks

Building blocks were synthesized according to the following general procedures. Further details as well as all modifications to the syntheses outlined below are described prior to the characterization of all associated compounds.



Scheme 1. General method of carbazole building blocks **7a**-**7e**.

***N*-Substitution of carbazole (2) –** A mixture of carbazole (1 equiv), the appropriate bromo substituted side chain (1.2 equiv.), and KOH (3 equiv.) in acetone was heated to reflux overnight. After removing the solvent in vacuo, the mixture was extracted with EtOAc and washed three times with a saturated brine solution. The organic layers were then combined, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude product was then subjected to column chromatography (SiO_2).

Nitration of *N*-substituted carbazole (3) – *N*-Substituted carbazole **2** was dissolved in 1,2-dichloroethane and cooled to 0°C in an ice bath. Concentrated nitric acid (16 M, 1.1 equiv.) was added dropwise to the cold solution with stirring. The reaction was subsequently heated to 60 °C and stirred for 3 h. After cooling to room temperature, deionized water was added and the mixture was extracted with three portions of CH_2Cl_2. The organic layers were combined, dried with $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude nitro-carbazole product was purified by either re-crystallization or column chromatography.

Iodination of 3-nitro-carbazole (4) – Nitro-substituted carbazole **3** was dissolved in $CHCl_3$ followed by slow addition of ICl (1.1 equiv.). The mixture was stirred at room temperature for 1 h, then heated at reflux for 30 min. The progress of the reaction was checked by ^1H NMR analysis. Upon completion, the reaction was quenched with a saturated aqueous solution of Na_2SO_3. The

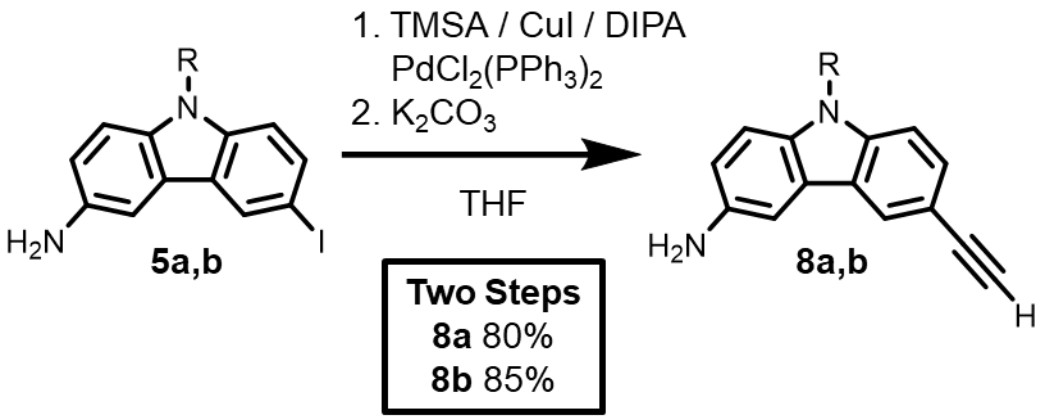
quenched reaction mixture was then extracted with three portions of CH_2Cl_2, the organic layers were combined, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude iodo-carbazole product was purified by either hot-filtration or column chromatography.

Reduction of 3-iodo-6-nitrocarbazole (5) – Difunctional carbazole **4** and $SnCl_2 \cdot 2H_2O$ (5 equiv.) were dissolved in a 1:1 mixture of ethyl acetate and ethanol which was then heated at reflux for 12 hours. After cooling to room temperature, the reaction mixture was poured into an aqueous solution of Na_2CO_3 and stirred for 2 h. The resulting slurry was filtered and then extracted with three portions of ethyl acetate. In some cases, the filtrate forms an emulsion that clears upon addition of ethanol. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude amino-carbazole product was purified by column chromatography.

Azidation of 3-amino-6-iodocarbazole (6) – Amino-carbazole **5** and *p*-toluenesulfonic acid monohydrate (3 equiv.) were dissolved in a 1:1 mixture of acetonitrile and THF and cooled to 0 °C using an ice bath. Upon cooling, the solution forms a dark brown slurry. A solution of $NaNO_2$ (1.1 equiv.) in water was added dropwise and the resulting mixture was stirred for 30 minutes. A solution of NaN_3 (1.2 equiv.) in water was added drop-wise, followed by stirring for an additional 30 minutes at 0°C. The mixture was warmed to room temperature and stirred for an additional 30 minutes. The mixture was basified with an aqueous NaOH solution (1 M) and extracted with three portions of ethyl acetate. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude azido-carbazole product was purified by column chromatography. ***NOTE*** Sodium azide (NaN_3) has similar levels of toxicity as sodium cyanide. Additionally, NaN_3 forms HN_3 gas, which is also toxic, upon treatment with strong acids. Further information and safety procedures can be found here.[S1]

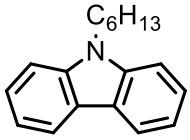
Sonogashira coupling of 3-azido-6-iodocarbazole (7-TMS) – Azido-carbazole **6** and diisopropylamine (5 equiv.) were dissolved in THF. The solution was then degassed with argon for 15 minutes before sequential addition of $PdCl_2(PPh_3)_2$ (0.02 equiv.), CuI (0.05 equiv.), and trimethylsilylacetylene (1.5 equiv.). The reaction mixture was stirred under an argon atmosphere for 40 min and quenched with an aqueous solution of NH_4Cl (1 M). The mixture was extracted with three portions of ethyl acetate. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting viscous oil was purified by column chromatography.

Desilylation of 3-azido-6-trimethylsilylethynylcarbazole (7) – TMS-protected carbazole **7-TMS** was dissolved in a 2:1 mixture of THF and methanol. A saturated solution of K_2CO_3 (0.25 M, 0.5 equiv.) in methanol was added and the mixture was stirred for one hour. The reaction was quenched with aqueous NH_4Cl (1 M) and extracted with three portions of CH_2Cl_2. The organic layers were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting compound was purified by column chromatography.

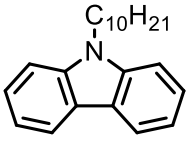


Scheme 2. Synthesis of carbazole building blocks **8a** and **8b**.

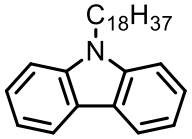
Sonogashira coupling of 3-amino-6-iodocarbazole (8) – Amino-carbazole **5** and diisopropylamine (5 equiv.) were dissolved in THF. The solution was degassed with argon for 15 minutes before sequential addition of $PdCl_2(PPh_3)_2$ (0.02 equiv.), CuI (0.05 equiv.), and trimethylsilylacetylene (1.5 equiv.). The reaction mixture was stirred under an argon atmosphere for 40 min and quenched with an aqueous solution of NH_4Cl (1 M). The mixture was extracted with three portions of ethyl acetate. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting intermediate was dissolved in a 2:1 mixture of THF and methanol. A saturated solution of K_2CO_3 in methanol (0.25 M, 0.5 equiv.) was added and the mixture stirred for one hour. The reaction was quenched with an aqueous NH_4Cl solution (1 M) and extracted with three portions of CH_2Cl_2. The organic layers were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude alkynyl-carbazole product was purified by column chromatography.



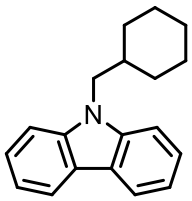
9-Hexylcarbazole (2a) – Compound **2a** was made following the general method of *N*-substituted carbazoles from carbazole (5 g, 30 mmol, 1 equiv.), 1-bromohexane (4.6 mL, 33 mmol, 1.1 equiv.), and KOH (5.5 g, 99 mmol, 3 equiv.). Following column chromatography on silica gel using hexanes as eluent, compound **2a** was recovered as a colorless, viscous oil (7.45 g, 29.6 mmol, 99%). The ^{1}H NMR spectrum was identical to previous reports.[S2]



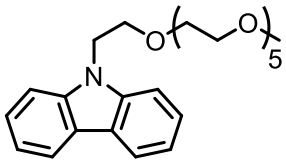
9-Decylcarbazole (2b) – Compound **2b** was synthesized following the general method of *N*-substituted carbazoles from carbazole (5 g, 30 mmol, 1 equiv.), 1-bromodecane (6.9 mL, 33 mmol, 1.1 equiv.), and KOH (5.5 g, 99 mmol, 3 equiv.). Following column chromatography on silica gel using hexanes as eluent, compound **2b** was recovered as a colorless, viscous oil (9.05 g, 29.5 mmol, 98%). The ^{1}H NMR spectrum was identical to previous reports.[S3]



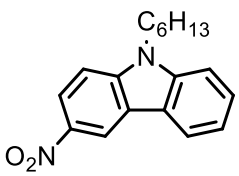
9-Octadecylcarbazole (2c) – Compound **2c** was made following the general method of *N*-substituted carbazoles from carbazole (5 g, 30 mmol, 1 equiv.), 1-bromooctadecane (11 g, 33 mmol, 1.1 equiv.), and KOH (5.5 g, 99 mmol, 3 equiv.). Following column chromatography on silica gel using hexanes as eluent, compound **2c** was recovered as a colorless, waxy solid (12.4 g, 29.6 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 7.48 (ddd, J = 8.2, 6.9, 1.2 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.24 (ddd, J = 7.9, 6.9, 1.2 Hz, 2H), 4.31 (t, J = 7.3 Hz, 2H), 1.89 (p, J = 8.0, 7.6 Hz, 2H), 1.57 – 1.12 (m, 30H), 0.90 (t, J = 6.9, 2.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.96, 125.52, 122.74, 120.29, 188.68, 109.09, 43.81, 31.98, 29.75, 29.73, 29.71, 29.67, 29.60, 29.55, 29.48, 29.41, 29.34, 28.89, 27.24, 22.75, 14.17 (three carbon peaks of the octadecyl chain are overlapping with others in the 31-28 ppm region). HRMS (EI) calcd for $C_{30}H_{45}N$: 419.3552 $[M]^+$; found: 419.3571.



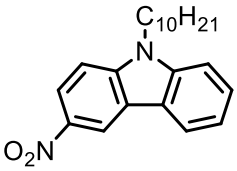
9-Methylcyclohexylcarbazole (2d) – Compound **2d** was prepared following the general method of *N*-substituted carbazoles from carbazole (5 g, 30 mmol, 1 equiv.), (bromomethyl)cyclohexane (4.6 ml, 33 mmol, 1.1 equiv.), and KOH (5.5 g, 99 mmol, 3 equiv.). Following column chromatography on silica gel using hexanes as eluent, compound **2d** was recovered as a colorless, waxy solid (7.8 g, 29.7 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 6.1 Hz, 2H), 7.48 (t, J = 6.2 Hz, 2H), 7.43 (d, J = 6.5 Hz, 2H), 7.24 (t, J = 6.0 Hz, 2H), 4.15 (d, J = 5.8 Hz, 2H), 2.12 – 1.96 (m, 1H), 1.79 – 1.63 (m, 5H), 1.29 – 1.06 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.89, 125.48, 122.69, 120.24, 118.64, 109.04, 49.65, 38.27, 31.52, 26.34, 25.84. HRMS (EI) calcd for $C_{19}H_{21}N$: 263.1674 $[M]^+$; found: 263.1684.



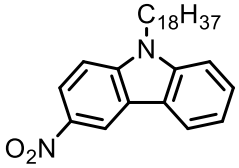
9-(2,5,8,11,14,17-Hexaoxanonadecan-19-yl)-carbazole (2e) – Compound **2a** was synthesized following the general method of *N*-substituted carbazoles from carbazole (5 g, 30 mmol, 1 equiv.), hexa(ethylene glycol) monomethyl ether tosylate (4.6 mL, 33 mmol, 1.1 equiv.), and KOH (5.5 g, 99 mmol, 3 equiv.). Following column chromatography on silica gel using ethyl acetate as eluent, compound **2e** was recovered as a colorless, viscous oil (12 g, 27 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 2H), 7.58 – 7.42 (m, 4H), 7.27 – 7.19 (m, peak partially overlaps with residual solvent peak), 4.53 (t, J = 6.0 Hz, 2H), 3.89 (t, J = 6.2 Hz, 2H), 3.71 – 3.49 (m, 20H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.58, 125.62, 122.90, 120.24, 118.97, 108.87, 71.94, 71.00, 70.60, 70.59, 70.55, 70.52, 70.51, 70.50, 69.28, 67.98, 61.74, 59.03, 43.15. HRMS (EI) calcd for $C_{25}H_{35}NO_6$+Na: 468.2357 $[M+Na]^+$; found: 468.2362.



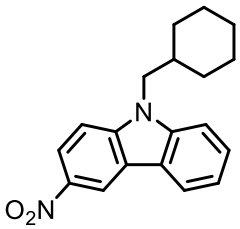
9-Hexyl-3-nitro-carbazole (3a) – Compound **3a** was prepared following the general method for the nitration of *N*-substituted carbazoles from carbazole **2a** (7.45 g, 29.6 mmol, 1 equiv.) and concentrated nitric acid (2 mL, 32.5 mmol, 1.1 equiv.). The crude nitro-carbazole **3a** was purified by recrystallization from hexanes to give pure product as a yellow solid (8.06 g, 27.2 mmol, 92%). The ^{1}H NMR spectrum was identical to previous reports.[S2]



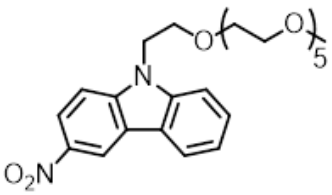
9-Decyl-3-nitro-carbazole (3b) – Compound **3b** was synthesized following the general method for the nitration of *N*-substituted carbazoles from carbazole **2b** (9.05 g, 29.5 mmol, 1 equiv.) and concentrated nitric acid (2 mL, 32.5 mmol, 1.1 equiv.). Crude nitro-carbazole **3b** was purified by recrystallization from hexanes to give pure product as a yellow solid (9.76 g, 27.7 mmol, 94%). The ^{1}H NMR spectrum was identical to previous reports.[S3]



3-Nitro-9-octadecyl-carbazole (3c) – Compound **3c** was prepared following the general method for the nitration of *N*-substituted carbazoles from carbazole **2c** (12.4 g, 29.6 mmol, 1 equiv.) and concentrated nitric acid (2 mL, 32.5 mmol, 1.1 equiv.). Crude nitro-carbazole **3c** was purified by column chromatography on SiO_2 using hexanes as eluent to give pure product as a yellow solid (13.06 g, 28.1 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J = 1.8 Hz, 1H), 8.41 (dd, J = 7.2, 1.8 Hz, 1H), 8.19 (d, J = 6.0 Hz, 1H), 7.59 (t, J = 6.3 Hz, 1H), 7.49 (d, J = 6.0 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 6.1 Hz, 1H), 4.37 (t, J = 5.8 Hz, 2H), 1.91 (p, J = 5.7 Hz, 2H), 1.46 – 1.06 (m, 30H), 0.90 (t, J = 5.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.99, 142.08, 140.54, 127.28, 122.77, 122.45, 121.55, 120.91, 120.69, 117.29, 110.08, 108.68, 50.09, 43.74, 31.93, 29.70, 29.66, 29.62, 29.56, 29.50, 29.41, 29.36, 29.28, 28.85, 27.18, 22.69, 14.12. HRMS (EI) calcd for $C_{30}H_{44}N_2O_2$+H: 465.3476 $[M+H]^+$; found: 465.3491.

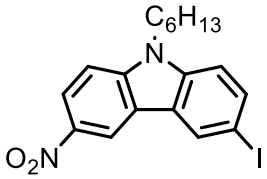


9-Methylcyclohexyl-3-nitro-carbazole (3d) – Compound **3d** was prepared following the general method for the nitration of *N*-substituted carbazoles from carbazole **2d** (7.8 g, 29.7 mmol, 1 equiv.) and concentrated nitric acid (2 mL, 32.5 mmol, 1.1 equiv.). Crude nitro-carbazole **3d** was purified by recrystallization from hexanes to give the product as a yellow solid (8.51 g, 27.6 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 2.0 Hz, 1H), 8.40 (dd, J = 7.3, 1.8 Hz, 1H), 8.18 (dd, J = 6.2, 0.8 Hz, 1H), 7.59 (ddd, J = 6.7, 5.7, 1.0 Hz, 1H), 7.50 (dd, J = 6.6, 0.7 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.37 (td, J = 6.1, 0.8 Hz, 1H), 4.19 (d, J = 5.9 Hz, 2H), 2.13 – 1.96 (m, 1H), 1.83 – 1.63 (m, 5H), 1.32 – 1.06 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.99, 142.08, 140.54, 127.28, 122.76, 122.44, 121.55, 120.91, 120.69, 117.28, 110.07, 108.67, 50.09, 38.21, 31.42, 26.17, 25.71. HRMS (EI) calcd for $C_{19}H_{20}N_2O_2$: 308.1525 $[M]^+$; found: 308.1547.

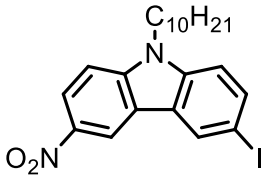


9-(2,5,8,11,14,17-Hexaoxanonadecan-19-yl)-3-nitro-carbazole (3e) – Compound **3e** was synthesized following the general method for the nitration of *N*-substituted carbazoles from carbazole **2e** (12 g, 27 mmol, 1 equiv.) and concentrated nitric acid (1.8 mL, 29.7 mmol, 1.1 equiv.). Crude nitro-carbazole **3c** was purified by column chromatography on silica gel using 2:1 ethyl acetate:hexanes as eluent to give pure product as a yellow solid (11.5 g, 23.5 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 1.8 Hz, 1H), 8.39 (dd, J = 7.2, 1.8 Hz, 1H), 8.17 (dt, J = 6.3, 0.8 Hz, 1H), 7.64 – 7.51

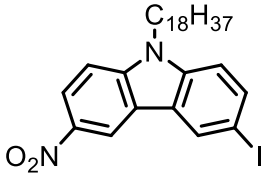
(m, 3H), 7.37 (ddd, J = 6.4, 5.5, 0.9 Hz, 1H), 4.57 (t, J = 4.5 Hz, 2H), 3.93 (t, J = 4.5 Hz, 2H), 3.71 – 3.59 (m, 10H), 3.59 – 3.48 (m, 10H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.02, 141.75, 140.76, 127.34, 122.90, 122.60, 121.53, 120.91, 120.89, 117.14, 109.85, 109.03, 71.93, 70.99, 70.62, 70.60, 70.55, 70.52, 70.51, 69.35, 59.02, 43.86. (four carbon peaks of the hexaethylene glycol chain are overlapping with others in the 70.70-70.40 ppm region). HRMS (EI) calcd for $C_{25}H_{34}N_2O_8$+Na: 513.2207 $[M+Na]^+$; found: 513.2237.



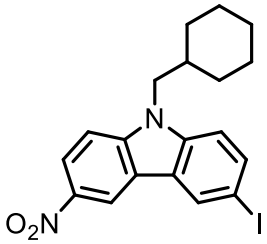
9-Hexyl-6-iodo-3-nitro-carbazole (4a) – Compound **4a** was made following the general method for the iodination of 3-nitro-carbazoles from nitro-carbazole **3a** (8.06 g, 27.2 mmol, 1 equiv.) and iodine monochloride (4.85 g, 29.9 mmol, 1.1 equiv.). Crude iodo-carbazole **4a** was purified by hot filtration from hexanes to give the product as a yellow solid (11.2 g, 26.6 mmol, 98%). The ^{1}H NMR spectrum was identical to previous reports.[S2]



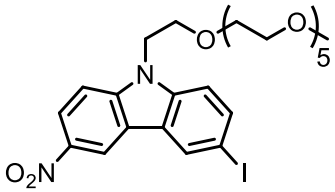
9-Decyl-6-iodo-3-nitro-carbazole (4b) – Compound **4b** was synthesized following the general method for the iodination of 3-nitro-carbazoles from nitro-carbazole **3b** (9.76 g, 27.7 mmol, 1 equiv.) and iodine monochloride (4.95 g, 30.5 mmol, 1.1 equiv.). Crude iodo-carbazole **4b** was purified by hot filtration from hexanes to give pure product as a yellow solid (11.91 g, 24.9 mmol, 90%). The ^{1}H NMR spectrum was identical to previous reports.[S3]



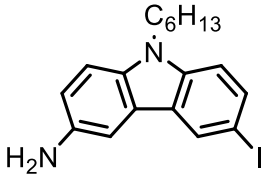
6-Iodo-3-nitro-9-octadecyl-carbazole (4c) – Compound **4c** was prepared following the general method for the iodination of 3-nitro-carbazoles from nitro-carbazole **3c** (13.06 g, 28.1 mmol, 1 equiv.) and iodine monochloride (5.01 g, 30.9 mmol, 1.1 equiv.). Crude iodo-carbazole **4c** was purified by hot filtration from hexanes to give product as a yellow solid (14.41 g, 24.4 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 1.7 Hz, 1H), 8.50 (d, J = 1.3 Hz, 1H), 8.42 (dd, J = 7.2, 1.7 Hz, 1H), 7.83 (dd, J = 6.8, 1.2 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.27 (s, overlaps with residual solvent peak), 4.34 (t, J = 5.8 Hz, 2H), 1.89 (p, J = 5.8 Hz, 2H), 1.46 – 1.15 (m, 30H), 0.90 (t, J = 5.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.34, 140.96, 140.81, 135.65, 129.88, 125.20, 122.16, 121.23, 117.51, 111.63, 108.54, 83.32, 43.74, 31.93, 29.70, 29.68, 29.66, 29.62, 29.56, 29.50, 29.42, 29.36, 29.28, 28.85, 27.19, 22.69, 14.12 (three carbon peaks of the octadecyl chain are overlapping with others in the 30-29 ppm region). HRMS (EI) calcd for $C_{30}H_{43}N_2O_2I$: 590.2369 $[M]^+$; found: 590.2399.



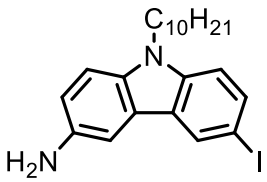
6-Iodo-9-methylcyclohexyl-3-nitro-carbazole (4d) – Compound **4d** was synthesized following the general method for the iodination of 3-nitro-carbazoles by starting with nitro-carbazole **3d** (8.51 g, 27.6 mmol, 1 equiv.) and iodine monochloride (4.94 g, 30.4 mmol, 1.1 equiv.). Crude iodo-carbazole **4c** was purified by hot filtration from hexanes to give pure product as a yellow solid (10.55 g, 24.3 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 1.7 Hz, 1H), 8.49 (d, J = 1.3 Hz, 1H), 8.41 (dd, J = 7.3, 1.9 Hz, 1H), 7.83 (dd, J = 6.9, 1.4 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.27 (peak partially overlaps with residual solvent peak), 4.16 (d, J = 5.9 Hz, 2H), 2.00 (dqd, J = 11.8, 6.1, 3.6 Hz, 1H), 1.83 – 1.60 (m, 5H), 1.28 – 1.05 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.79, 141.27, 140.93, 135.60, 129.78, 125.09, 122.10, 121.13, 117.44, 112.04, 108.97, 83.31, 53.42, 50.16, 38.17, 31.37, 26.11, 25.66. HRMS (EI) calcd for $C_{19}H_{19}N_2O_2I$: 434.0491 $[M]^+$; found: 434.0517.



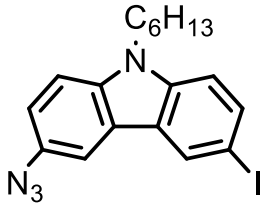
9-(2,5,8,11,14,17-Hexaoxanonadecan-19-yl)-6-iodo-3-nitro-carbazole (4e) – Compound **4e** was synthesized following the general method for the iodination of 3-nitro-carbazoles from nitro-carbazole **3e** (11.5 g, 23.5 mmol, 1 equiv.) and iodine monochloride (4.20 g, 25.9 mmol, 1.1 equiv.). Crude iodo-carbazole **4e** was purified by column chromatography on silica gel with 2:1 ethyl acetate:hexanes as eluent to give the product as a yellow solid (11.71 g, 19.0 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 1.8 Hz, 1H), 8.48 (d, J = 1.0 Hz, 1H), 8.40 (dd, J = 7.2, 1.8 Hz, 1H), 7.82 (dd, J = 6.8, 1.4 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.35 (d, J = 6.9 Hz, 1H), 4.54 (t, J = 4.4 Hz, 2H), 3.91 (t, J = 4.3 Hz, 2H), 3.69 – 3.59 (m, 10H), 3.58 – 3.46 (m, 10H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.81, 141.13, 141.07, 135.62, 129.73, 125.22, 122.07, 121.30, 117.30, 112.04, 109.28, 83.51, 71.93, 70.97, 70.62, 70.60, 70.56, 70.54, 70.51, 70.50, 69.35, 59.03, 44.04 (three carbon peaks of the hexaethylene glycol chain are overlapping with others in the 70.70-70.40 ppm region). HRMS (EI) calcd for $C_{25}H_{33}N_2O_8I$+Na: 639.1174 $[M+Na]^+$; found: 639.1202.



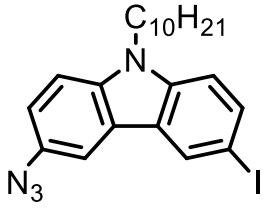
3-Amino-9-hexyl-6-iodo-carbazole (5a) – Compound **5a** was prepared following the general method for the reduction of 3-nitro-6-iodo-carbazoles from iodo-carbazole **4a** (11.2 g, 26.6 mmol, 1 equiv.) and $SnCl_2$•2 H_2O (30 g, 133 mmol, 5 equiv.). The crude amino-carbazole **5a** was purified by column chromatography on silica gel with dichloromethane as eluent to give pure product as a yellow-brown solid (8.35 g, 21.3 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.8 Hz, 1H), 7.65 (dd, J = 8.6, 1.8 Hz, 1H), 7.36 (d, J = 2.3 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 7.14 (d, J = 8.6 Hz, 1H), 6.94 (dd, J = 8.6, 2.3 Hz, 1H), 4.21 (t, J = 7.3 Hz, 2H), 3.66 (s, 2H), 1.81 (p, J = 7.3 Hz, 2H), 1.44 – 1.24 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.95, 139.30, 134.98, 133.50, 129.14, 124.87, 122.29, 116.28, 110.65, 109.46, 106.06, 80.12, 43.19, 31.55, 28.92, 26.92, 22.53, 14.00. HRMS (EI) calcd for $C_{18}H_{21}N_2I$+H: 393.0822 $[M+H]^+$; found: 393.0831.



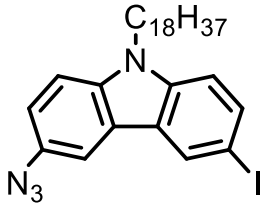
3-Amino-9-decyl-6-iodo-carbazole (5b) – Compound **5b** was synthesized following the general method for the reduction of 3-nitro-6-iodo-carbazoles from iodo-carbazole **4b** (11.91 g, 24.9 mmol, 1 equiv.) and $SnCl_2$•2 H_2O (28.1 g, 124.5 mmol, 5 equiv.). Crude amino-carbazole **5b** was purified by column chromatography on SiO_2 with dichloromethane as eluent to give the product as a yellow-brown solid (8.92 g, 19.9 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.7 Hz, 1H), 7.65 (dd, J = 8.6, 1.7 Hz, 1H), 7.36 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 7.14 (d, J = 8.6 Hz, 1H), 6.94 (dd, J = 8.6, 2.3 Hz, 1H), 4.20 (t, J = 7.2 Hz, 2H), 3.66 (s, 2H), 1.82 (p, J = 6.9 Hz, 2H), 1.50 – 1.15 (m, 14H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.28, 133.45, 129.10, 116.22, 110.62, 109.42, 106.00, 43.15, 31.81, 29.47, 29.34, 29.22, 28.90, 27.23, 22.63, 14.08. HRMS (EI) calcd for $C_{22}H_{29}N_2I$+H: 449.1448 $[M+H]^+$; found: 449.1465.



3-Azido-9-hexyl-6-iodo-carbazole (6a) – Compound **6a** was made following the general method for the azidation of amino-carbazoles from amino-carbazole **5a** (8.35 g, 21.3 mmol, 1 equiv.), *p*-toluenesulfonic acid monohydrate (12.15 g, 63.9 mmol, 3 equiv.), sodium nitrite (1.61 g, 23.4 mmol, 1.1 equiv.), and sodium azide (1.66 g, 25.5 mmol, 1.2 equiv.). Crude azido-carbazole **6a** was purified by column chromatography on silica gel with 97:3 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (8.45 g, 20.2 mmol, 95%). The ^{1}H NMR spectrum was identical to previous reports.[S2]

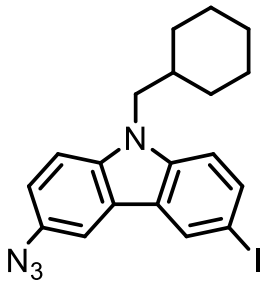


3-Azido-9-decyl-6-iodo-carbazole (6b) – Compound **6b** was synthesized following the general method for the azidation of amino-carbazoles from amino-carbazole **5b** (8.92 g, 19.9 mmol, 1 equiv.), *p*-toluenesulfonic acid monohydrate (11.36 g, 59.7 mmol, 3 equiv.), sodium nitrite (1.61 g, 21.8 mmol, 1.1 equiv.), and sodium azide (1.66 g, 25.5 mmol, 1.2 equiv.). Crude azido-carbazole **6a** was purified by column chromatography on silica gel with 97:3 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (8.97 g, 18.9 mmol, 95%). The ^{1}H NMR spectrum was identical to previous reports.[S3]

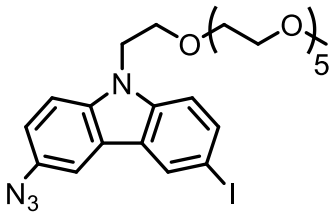


3-Azido-6-iodo-9-octadecyl-carbazole (6c) – Compound **6c** was prepared by first following the general method for the reduction of 3-nitro-6-iodo-carbazoles from iodo-carbazole **4c** (14.41 g, 24.4 mmol, 1 equiv.) and $SnCl_2$•2 H_2O (27.5 g, 122 mmol, 5 equiv.). The crude amino-carbazole **5c** was used immediately without further purification. Then, the general procedure for the azidation of nitro-carbazole was conducted with intermediate amino-carbazole **5c** along with *p*-toluenesulfonic acid monohydrate (13.9 g, 73.2 mmol, 3 equiv.), sodium nitrite (1.84 g, 26.6 mmol, 1.1 equiv.), and sodium azide (1.9 g, 29.3 mmol, 1.2 equiv.). Crude azido-carbazole **6c** was purified by column chromatography on silica gel with 97:3 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (10.85 g, 18.5 mmol, 76% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 1.7 Hz, 1H), 7.72 (dd, J = 8.7, 1.8 Hz, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.17 (dd, J = 9.5, 7.5 Hz, 2H),

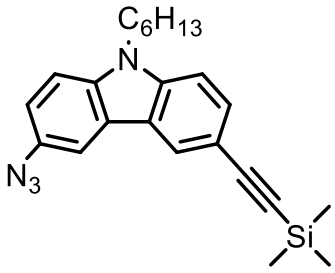
4.24 (t, *J* = 7.2 Hz, 2H), 1.84 (p, *J* = 6.9, 6.4 Hz, 2H), 1.42 – 1.18 (m, 30H), 0.98 – 0.83 (m, 3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.07, 137.89, 134.37, 131.58, 129.35, 124.44, 122.37, 117.94, 110.95, 110.31, 109.90, 81.21, 43.31, 31.88, 29.55, 29.49, 29.42, 29.30, 29.29, 28.86, 27.19, 22.66, 22.29, 14.10. (six carbon peaks of the octadecyl chain are overlapping with others in the 30-29 ppm region). HRMS (EI) calcd for $C_{30}H_{43}N_4I$: 586.2532 $[M]^+$; found: 586.2554.



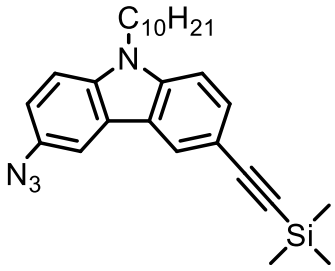
3-Azido-6-iodo-9-methylcyclohexyl-carbazole (6d) – Compound **6d** was synthesized by following the general method for the reduction of 3-nitro-6-iodo-carbazoles from iodo-carbazole **4d** (10.55 g, 24.3 mmol, 1 equiv.) and $SnCl_2$•2 H_2O (27.4 g, 121.5 mmol, 5 equiv.). The crude amino-carbazole **5c** was then used immediately without further purification. The general procedure for azidation of nitro-carbazole was conducted on intermediate amino-carbazole **5d** along with *p*-toluenesulfonic acid monohydrate (13.87 g, 72.9 mmol, 3 equiv.), sodium nitrite (1.84 g, 26.7 mmol, 1.1 equiv.), and sodium azide (1.9 g, 29.2 mmol, 1.2 equiv.). Crude azido-carbazole **6d** was purified by column chromatography on SiO_2 with 97:3 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (6.31 g, 14.7 mmol, 60% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 1.3 Hz, 1H), 7.72 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.16 (dd, *J* = 7.0, 1.8 Hz, 1H), 4.09 (d, *J* = 5.9 Hz, 2H), 1.97 (ddq, *J* = 8.8, 5.7, 3.0 Hz, 1H), 1.80 – 1.59 (m, 5H), 1.27 – 1.02 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.59, 138.40, 134.37, 131.62, 129.32, 124.38, 122.31, 117.95, 111.40, 110.34, 110.28, 81.23, 49.85, 38.22, 31.41, 26.22, 25.74. HRMS (EI) calcd for $C_{19}H_{19}N_4I$: 430.0654 $[M]^+$; found: 430.0665.



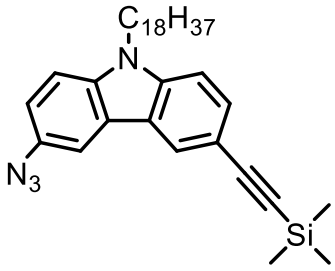
3-Azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-iodo-carbazole (6e) – Compound **6e** was synthesized by first following the general method for the reduction of 3-nitro-6-iodo-carbazoles by using iodo-carbazole **4e** (11.71 g, 19.0 mmol, 1 equiv.) with $SnCl_2$•2 H_2O (21.4 g, 95 mmol, 5 equiv.). The crude amino-carbazole **5e** was used without further purification. The general procedure for azidation of nitro-carbazole was conducted with the intermediate **5e** along with *p*-toluenesulfonic acid monohydrate (10.84 g, 57 mmol, 3 equiv.), sodium nitrite (1.44 g, 20.9 mmol, 1.1 equiv.), and sodium azide (1.48 g, 22.8 mmol, 1.2 equiv.). Crude azido-carbazole **6e** was purified by column chromatography on silica gel with 4:1 ethyl acetate:acetone as eluent to give the product as a light brown solid (8.96 g, 14.6 mmol, 77% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.26 (d, peak partially overlaps with residual solvent peak), 7.15 (d, *J* = 8.7 Hz, 1H), 4.46 (t, *J* = 5.7 Hz, 2H), 3.85 (t, *J* = 5.7 Hz, 2H), 3.72 – 3.61 (m, 10H), 3.58 – 3.46 (m, 10H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.13, 137.94, 134.40, 131.63, 129.41, 124.48, 122.42, 117.99, 110.99, 110.37, 109.93, 81.25, 71.98, 71.02, 70.65, 70.64, 70.60, 70.59, 70.56, 70.55, 69.41, 59.08, 44.09. HRMS (EI) calcd for $C_{25}H_{33}N_4O_6I$+Na: 635.1337 $[M+Na]^+$; found: 635.1350.



3-Azido-9-hexyl-6-((trimethylsilyl)ethynyl)-carbazole (7a-TMS) – Compound **7a-TMS** was synthesized following the general method for the Sonogashira coupling of 3-azido-6-iodo-carbazoles using azido-carbazole **6a** (8.45 g, 20.2 mmol, 1 equiv.), diisopropylamine (14.1 mL, 101 mmol, 5 equiv.), copper iodide (192 mg, 1.01 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (281 mg, 0.40 mmol, 0.02 equiv.), and trimethylsilylacetylene (4.2 mL, 30.3 mmol, 1.5 equiv.). Crude carbazole **7a-TMS** was purified by column chromatography on silica gel with 98:2 hexanes:ethyl acetate as eluent to give pure product as a viscous brown oil (6.30 g, 16.2 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.60 (dd, J = 6.7, 1.1 Hz, 1H), 7.38 (d, J = 6.9 Hz, 1H), 7.32 (d, J = 6.8 Hz, 1H), 7.16 (dd, J = 7.0, 1.8 Hz, 1H), 4.28 (t, J = 5.8 Hz, 2H), 1.86 (p, J = 5.8 Hz, 2H), 1.43 – 1.22 (m, 6H), 0.88 (t, J = 5.6 Hz, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.73, 138.34, 131.68, 130.13, 124.77, 123.42, 121.86, 117.69, 113.37, 110.40, 109.97, 108.82, 106.31, 92.00, 43.38, 31.50, 28.91, 26.89, 22.51, 13.96, 0.17. HRMS (EI) calcd for $C_{23}H_{28}N_4Si$: 388.2083 $[M]^+$; found: 388.2092.

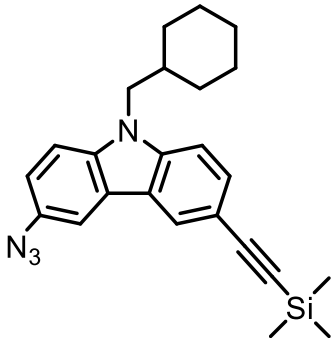


3-Azido-9-decyl-6-((trimethylsilyl)ethynyl)-carbazole (7b-TMS) – Compound **7b-TMS** was prepared by following the general method for the Sonogashira coupling of 3-azido-6-iodo-carbazoles from azido-carbazole **6b** (8.97 g, 18.9 mmol, 1 equiv.), diisopropylamine (13.2 mL, 94.5 mmol, 5 equiv.), copper iodide (181 mg, 0.95 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (273 mg, 0.39 mmol, 0.02 equiv.), and trimethylsilylacetylene (3.9 mL, 28.4 mmol, 1.5 equiv.). The crude carbazole **7b-TMS** was purified by column chromatography on silica gel with 98:2 hexanes:ethyl acetate as eluent to give the product as a viscous brown oil (7.16 g, 16.1 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 1.5 Hz, 1H), 7.72 (d, J = 2.2 Hz, 1H), 7.59 (dd, J = 8.5, 1.7 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.15 (dd, J = 8.6, 2.3 Hz, 1H), 4.26 (t, J = 7.2 Hz, 2H), 2.05 – 1.74 (m, 2H), 1.49 – 1.09 (m, 14H), 0.89 (t, J = 6.8 Hz, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.79, 138.39, 131.73, 130.19, 124.81, 123.47, 121.91, 117.75, 113.41, 110.46, 110.02, 108.86, 106.38, 92.06, 43.20, 31.87, 29.53, 29.50, 29.40, 29.26, 28.96, 27.28, 22.68, 14.14, 0.23. HRMS (EI) calcd for $C_{27}H_{36}N_4Si$: 444.2709 $[M]^+$; found: 444.2730.

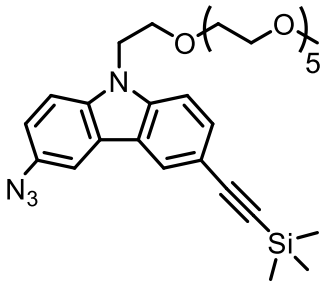


3-Azido-9-octadecyl-6-((trimethylsilyl)ethynyl)-carbazole (7c-TMS) – Compound **7c-TMS** was synthesized following the general method for Sonogashira coupling of 3-azido-6-iodo-carbazoles from azido-carbazole **6c** (10.85 g, 18.5 mmol, 1 equiv.), diisopropylamine (13.0 mL, 92.5 mmol, 5 equiv.), copper iodide (177 mg, 0.93 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (260 mg, 0.37 mmol, 0.02 equiv.), and trimethylsilylacetylene (3.8 mL, 27.8 mmol, 1.5 equiv.). Carbazole **7c-TMS** was purified by column chromatography on silica gel with 98:2 hexanes:ethyl acetate as eluent to give pure product as a viscous brown oil (8.24 g, 14.8 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 1.4 Hz, 1H), 7.72 (d, J = 2.2 Hz, 1H), 7.59 (dd, J = 8.5, 1.6 Hz, 1H), 7.37 (d, J = 8.9 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.16 (dd, J = 8.7, 2.1 Hz,

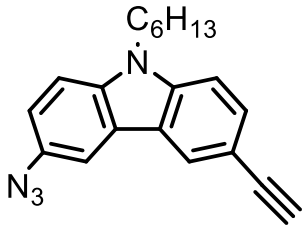
1H), 4.27 (t, *J* = 7.2 Hz, 2H), 1.83 (dt, *J* = 14.3, 6.7 Hz, 2H), 1.41 – 1.15 (m, 30H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.30 (d, *J* = 1.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.78, 138.39, 131.74, 130.19, 124.81, 123.46, 121.89, 117.74, 113.42, 110.45, 110.02, 108.87, 106.37, 92.05, 43.79, 31.96, 29.75, 29.71, 29.68, 29.60, 29.54, 29.47, 29.40, 29.34, 28.89, 27.24, 22.74, 14.16, 0.21. HRMS (EI) calcd for $C_{35}H_{52}N_4Si$: 556.3961 $[M]^+$; found: 556.3962.



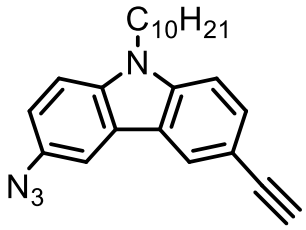
3-Azido-9-methylcyclohexyl-6-((trimethylsilyl)ethynyl)-carbazole (7d-TMS) – Compound **7d-TMS** was made following the general method for the Sonogashira coupling of 3-azido-6-iodo-carbazoles from azido-carbazole **6d** (6.31 g, 14.7 mmol, 1 equiv.), diisopropylamine (10.3 mL, 73.5 mmol, 5 equiv.), copper iodide (140 mg, 0.735 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (206 mg, 0.294 mmol, 0.02 equiv.), and trimethylsilylacetylene (3.1 mL, 22.05 mmol, 1.5 equiv.). Crude carbazole **7d-TMS** was purified by column chromatography (SiO_2) with 98:2 hexanes:ethyl acetate as eluent to give the pure product as a viscous brown oil (4.13 g, 10.3 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.08 (d, *J* = 7.3 Hz, 2H), 1.97 (ddt, *J* = 10.6, 6.6, 3.4 Hz, 1H), 1.77 – 1.60 (m, 5H), 1.27 – 1.01 (m, 5H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.18, 138.80, 131.65, 130.06, 124.68, 123.30, 121.76, 117.64, 113.36, 110.38, 110.30, 109.24, 106.30, 92.02, 49.87, 38.23, 31.41, 26.23, 25.74, 0.17. HRMS (EI) calcd for $C_{24}H_{28}N_4Si$: 400.2083 $[M]^+$; found: 400.2113.



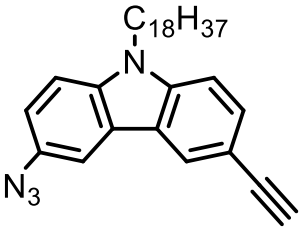
3-Azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-((trimethylsilyl)ethynyl)-carbazole (7e-TMS) – Compound **7e-TMS** was synthesized following the general method for the Sonogashira coupling of 3-azido-6-iodo-carbazoles from azido-carbazole **6e** (8.96 g, 14.6 mmol, 1 equiv.), diisopropylamine (10.2 mL, 73 mmol, 5 equiv.), copper iodide (139 mg, 0.73 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (204 mg, 0.29 mmol, 0.02 equiv.), and trimethylsilylacetylene (3 mL, 21.9 mmol, 1.5 equiv.). Crude carbazole **7e-TMS** was purified by column chromatography on silica gel with ethyl acetate as eluent to give the product as a viscous brown oil (7.23 g, 12.4 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.03 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.55 (m, 2H), 7.23 (d, *J* = 6.8 Hz, 1H), 4.61 (t, *J* = 5.4 Hz, 2H), 3.93 (t, *J* = 5.3 Hz, 2H), 3.68 – 3.39 (m, 20H), 3.32 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.83, 138.44, 131.77, 130.25, 124.87, 123.52, 121.95, 117.79, 113.46, 110.50, 110.08, 108.90, 106.41, 92.10, 71.99, 71.03, 70.67, 70.64, 70.59, 70.58, 70.55, 70.54, 69.40, 59.07, 44.08, 0.24. HRMS (EI) calcd for $C_{30}H_{42}N_4O_6Si$+Na: 605.2766 $[M+Na]^+$; found: 605.2789.



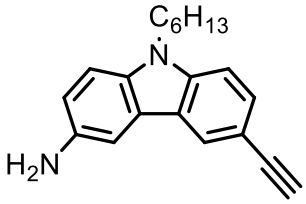
3-Azido-9-hexyl-6-ethynyl-carbazole (7a) – Alkynyl-carbazole **7a** was synthesized following the general procedure for the desilylation of 3-azido-6-trimethylsilylethynylcarbazole from compound **7a-TMS** (6.30 g, 16.2 mmol, 1 equiv.) and a saturated solution of K_2CO_3 in methanol (30 mL, 0.25 M, 0.5 equiv.). Crude alkyne **7a** was purified by column chromatography on silica gel with 98:2 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (5.09 g, 16.1 mmol, 99%). The ^{1}H NMR spectrum was identical to previous reports.[S2]



3-Azido-9-decyl-6-ethynyl-carbazole (7b) – Alkynyl-carbazole **7b** was synthesized following the general method for desilylation from compound **7b-TMS** (7.16 g, 16.1 mmol, 1 equiv.) using a saturated solution of K_2CO_3 in methanol (30 mL, 0.25 M, 0.5 equiv.). Alkyne **7b** was purified by column chromatography on silica gel with 98:2 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (5.92 g, 15.9 mmol, 99%). The ^{1}H NMR spectrum was identical to previous reports.[S3]

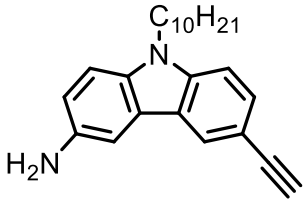


3-Azido-9-octadecyl-6-ethynyl-carbazole (7c) – Alkynyl-carbazole **7c** was synthesized following the general desilylation procedure of compound **7c-TMS** (8.24 g, 14.8 mmol, 1 equiv.) with a saturated solution of K_2CO_3 in methanol (29 mL, 0.25 M, 0.5 equiv.). Crude alkyne **7c** was purified by column chromatography (SiO_2) with 98:2 hexanes:ethyl acetate as eluent to give pure product as a light brown solid (6.98 g, 14.4 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.60 (dd, J = 8.5, 1.6 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.15 (dd, J = 8.7, 2.3 Hz, 1H), 4.25 (t, J = 7.2 Hz, 2H), 1.85 (p, J = 6.5 Hz, 2H), 1.40 – 1.20 (m, 30H), 0.92 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.90, 138.40, 131.77, 130.22, 124.94, 123.34, 121.97, 117.83, 112.32, 110.50, 110.04, 109.0, 84.78, 75.40, 50.14, 43.79, 31.99, 29.75, 29.72, 29.68, 29.62, 29.55, 29.47, 29.42, 29.32, 28.88, 27.24, 22.74, 14.18. HRMS (EI) calcd for $C_{32}H_{44}N_4$: 484.3566 $[M]^+$; found: 484.3592.



3-Amino-6-ethynyl-9-hexyl-carbazole (8a) – Combound **8a** was prepared following the general procedure for the Sonogashira coupling of 3-amino-6-iodocarbazole using amino-carbazole **5a** (4 g, 10.2 mmol, 1 equiv.), diisopropylamine (7.1 mL, 51 mmol, 5 equiv.), copper iodide (97 mg, 0.51 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (143 mg, 0.20 mmol, 0.02 equiv.), and trimethylsilylacetylene (2.1 mL, 15.3 mmol, 1.5 equiv.). Crude carbazole **8a** was purified by column chromatography on silica gel with dichloromethane as eluent to give the product as a light brown solid (80% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 1.5 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.28 (d, J = 8.3 Hz, overlaps with residual solvent peak), 7.23 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 4.23 (t, 2H), 3.68 (s, 2H), 3.07 (s, 1H), 1.84 (p, J = 7.0 Hz, 2H), 1.50 – 1.20 (m,

6H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.70, 139.43, 135.28, 129.36, 124.68, 123.11, 122.18, 115.98, 111.00, 109.51, 108.52, 106.14, 85.30, 74.77, 43.22, 31.54, 28.95, 26.92, 22.52, 13.98. HRMS (EI) calcd for $C_{20}H_{22}N_2$+H: 291.1856 $[M+H]^+$; found: 291.1858.



3-Amino-9-decyl-6-ethynyl-carbazole (8b) – Combound **8b** was synthesized following the general procedure for Sonogashira coupling amino-carbazole **5b** (4 g, 8.9 mmol, 1 equiv.), diisopropylamine (6.2 mL, 44.5 mmol, 5 equiv.), copper iodide (86 mg, 0.45 mmol, 0.05 equiv.), $PdCl_2(PPh_3)_2$ (126 mg, 0.18 mmol, 0.02 equiv.), and trimethylsilylacetylene (1.9 mL, 13.4 mmol, 1.5 equiv.). Carbazole **8b** was purified by column chromatography on silica gel with dichloromethane as eluent to give pure product as a light brown solid (2.63 g, 7.6 mmol, 85% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 1.7 Hz, 1H), 7.65 (dd, J = 8.6, 1.7 Hz, 1H), 7.35 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 8.6 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 6.94 (dd, J = 8.6, 2.3 Hz, 1H), 4.20 (t, J = 7.2 Hz, 2H), 3.64 (s, 2H), 1.82 (p, J = 7.0 Hz, 2H), 1.53 – 1.11 (m, 14H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.67, 139.41, 135.25, 129.34, 124.65, 123.09, 122.15, 115.95, 110.97, 109.49, 108.49, 106.11, 85.27, 74.74, 43.15, 31.81, 29.47, 29.45, 29.34, 29.22, 28.90, 27.22, 22.63, 14.08. HRMS (EI) calcd for $C_{24}H_{30}N_2$+H: 347.2482 $[M+H]^+$; found: 347.2493.

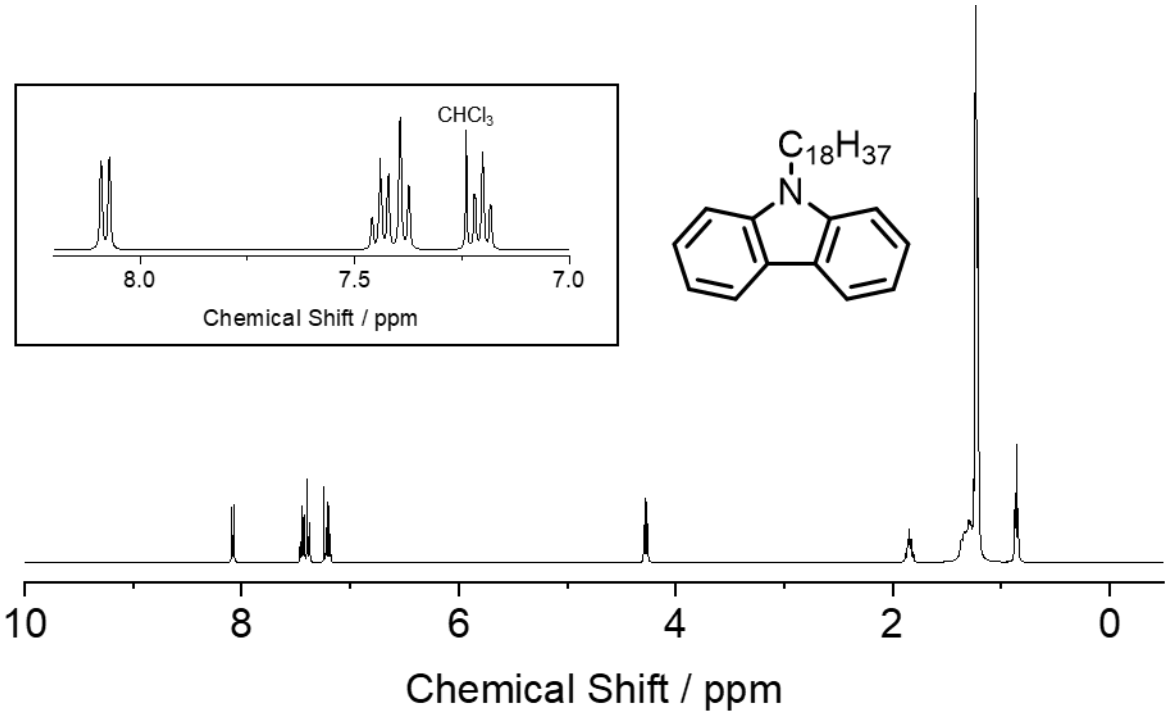


Figure S1. ^{1}H NMR spectrum of 9-octadecylcarbazole (**2c**).

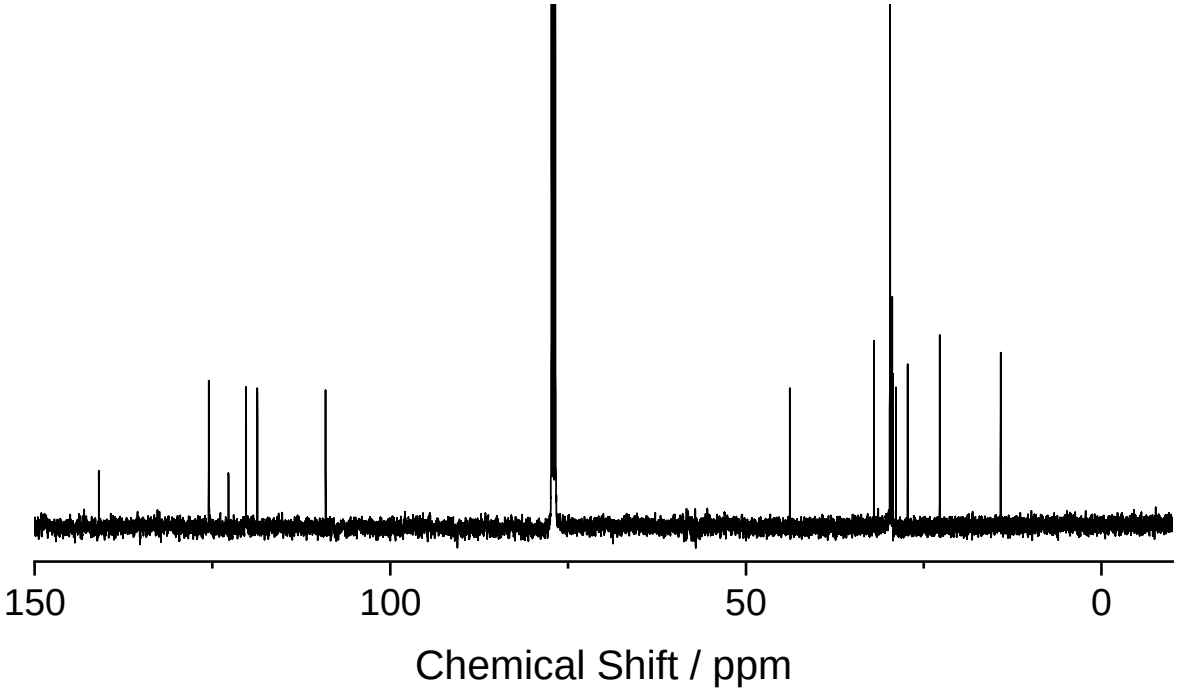


Figure S2. ^{13}C NMR spectrum of 9-octadecylcarbazole (**2c**).

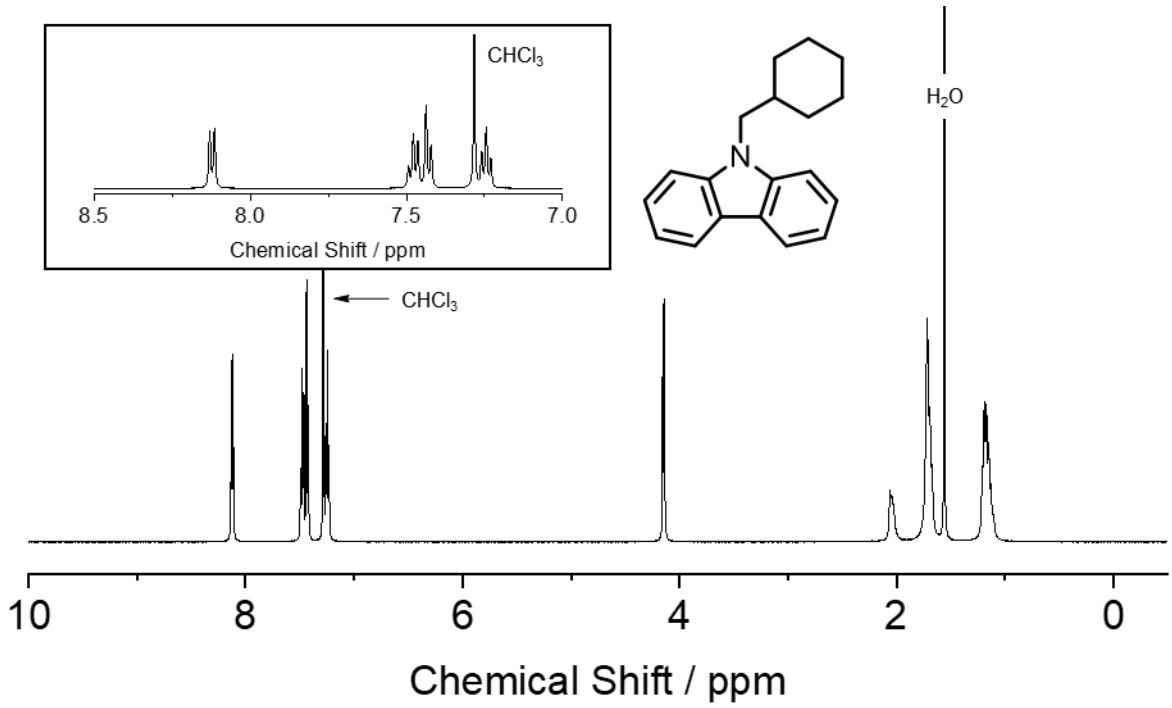


Figure S3. ^{1}H NMR spectrum of 9-methylcyclohexylcarbazole (**2d**).

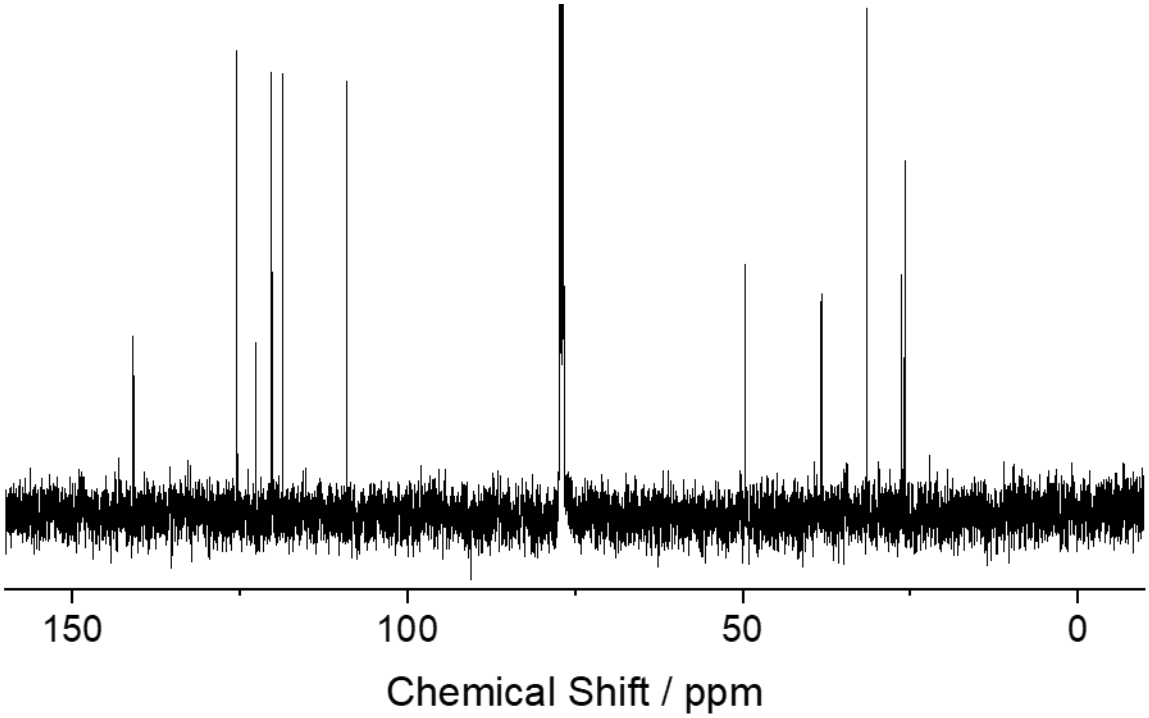


Figure S4. ^{13}C NMR spectrum of 9-methylcyclohexylcarbazole (**2d**).

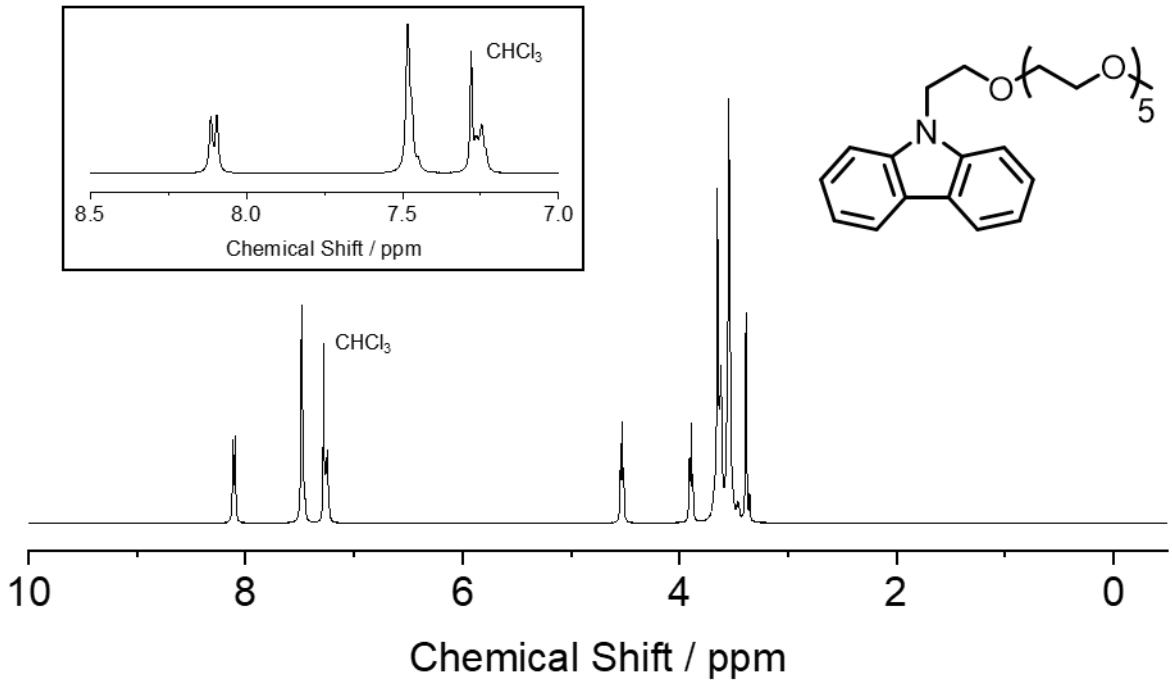


Figure S5. ^{1}H NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-carbazole (**2e**).

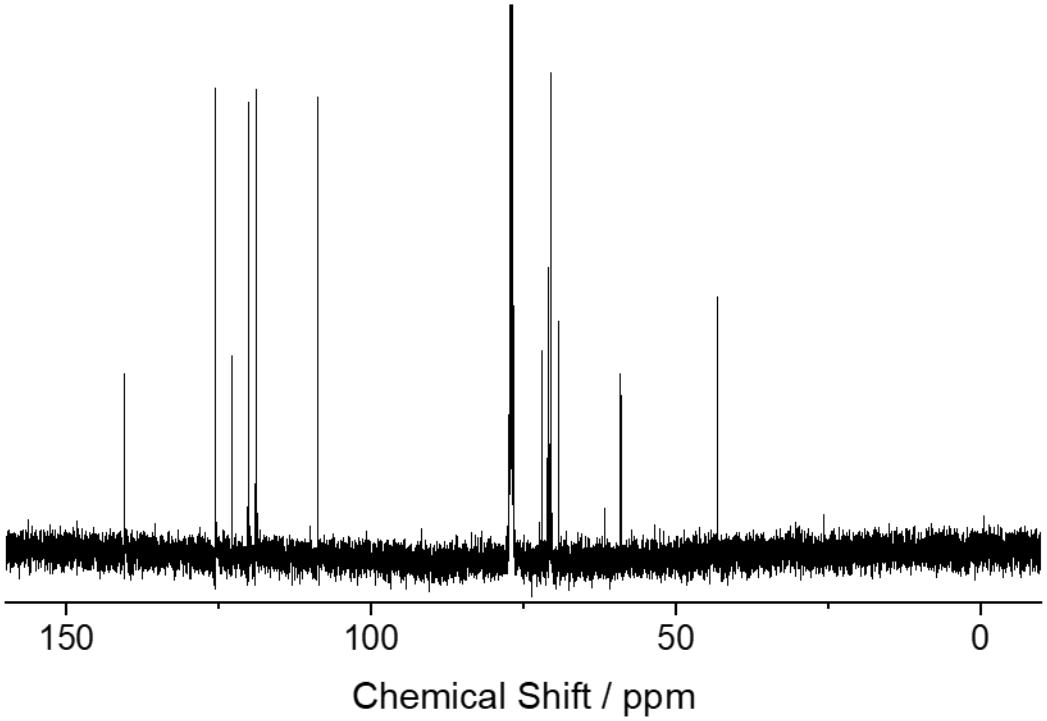


Figure S6. ^{13}C NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-carbazole (**2e**).

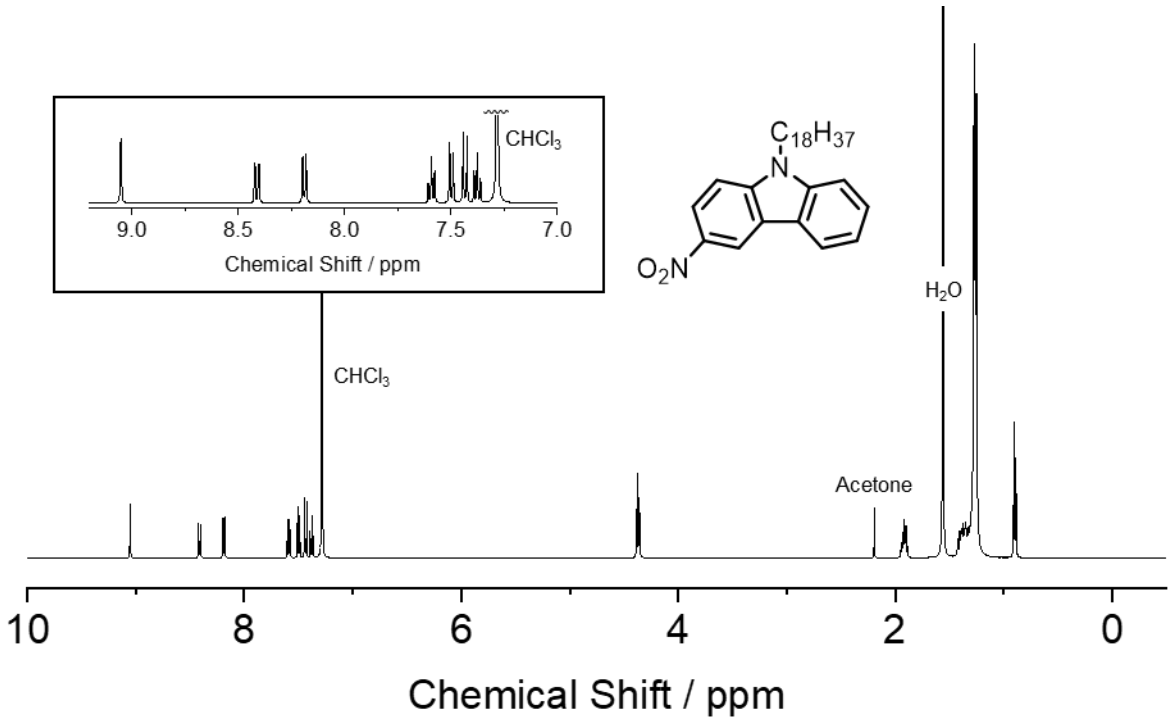


Figure S7. ^{1}H NMR spectrum of 3-nitro-9-octadecyl-carbazole (**3c**).

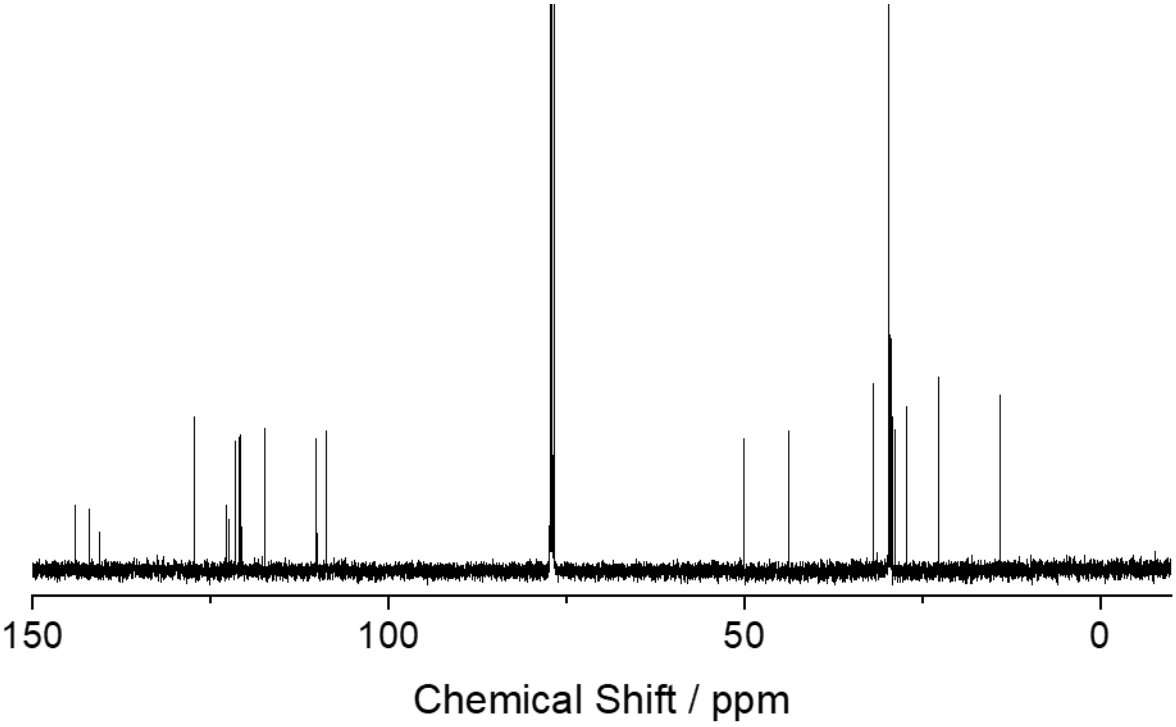


Figure S8. ^{13}C NMR spectrum of 3-nitro-9-octadecyl-carbazole (**3c**).

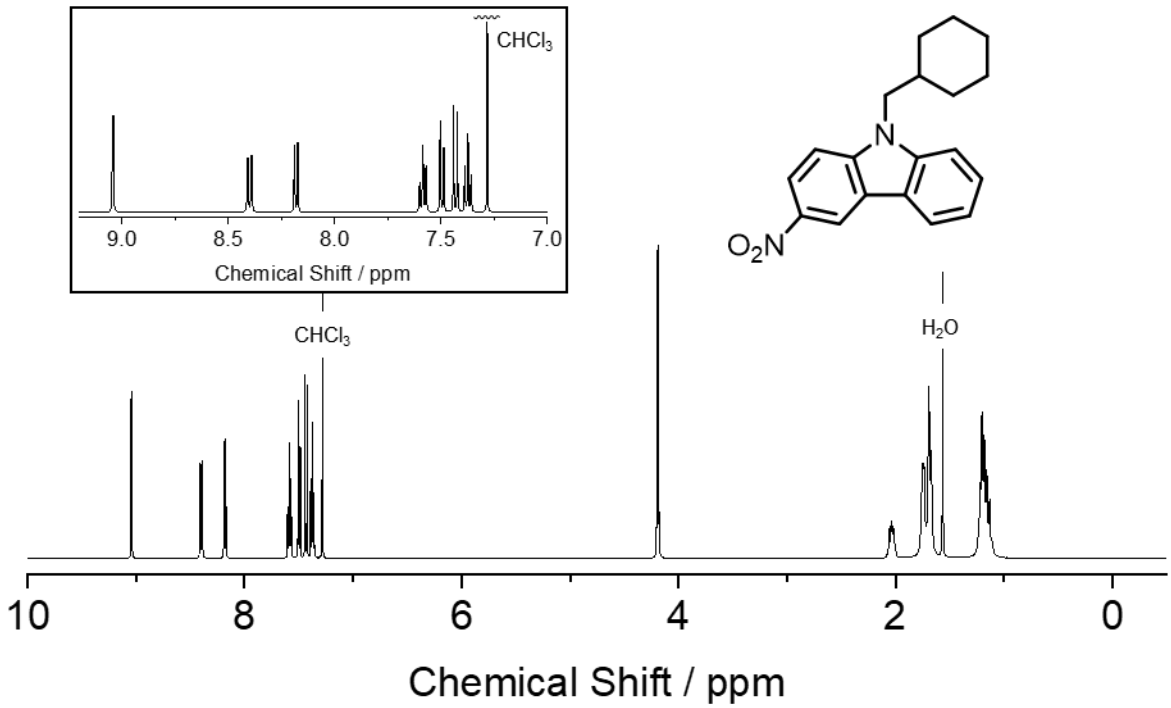


Figure S9. ^{1}H NMR spectrum of 9-methylcyclohexyl-3-nitro-carbazole (**3d**).

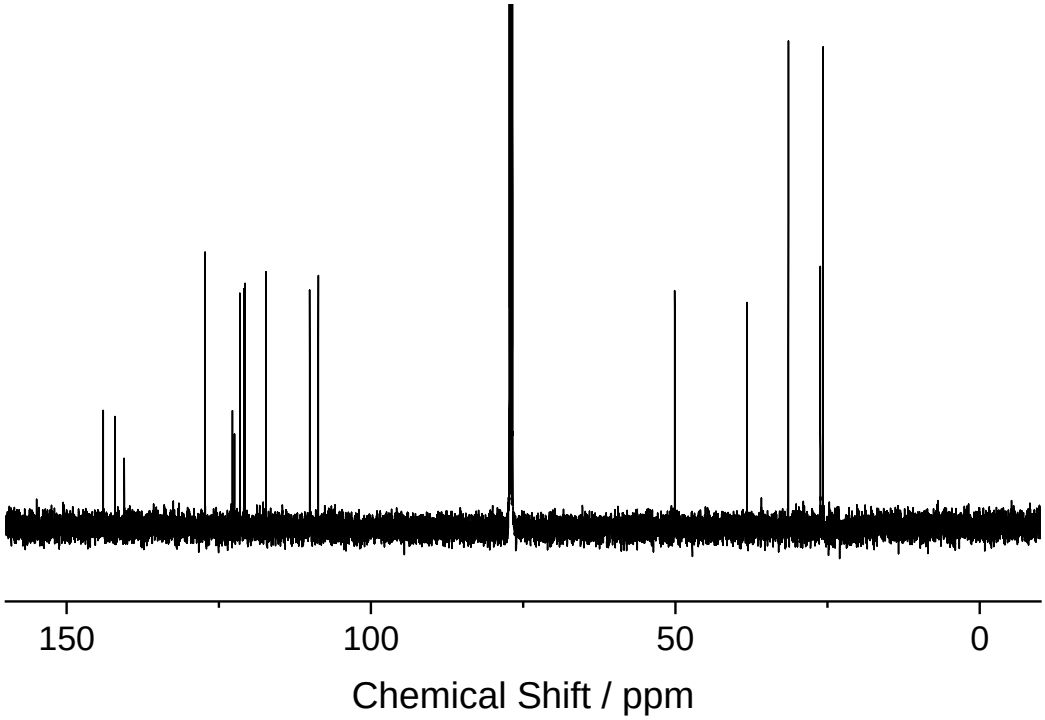


Figure S10. ^{13}C NMR spectrum of 9-methylcyclohexyl-3-nitro-carbazole (**3d**).

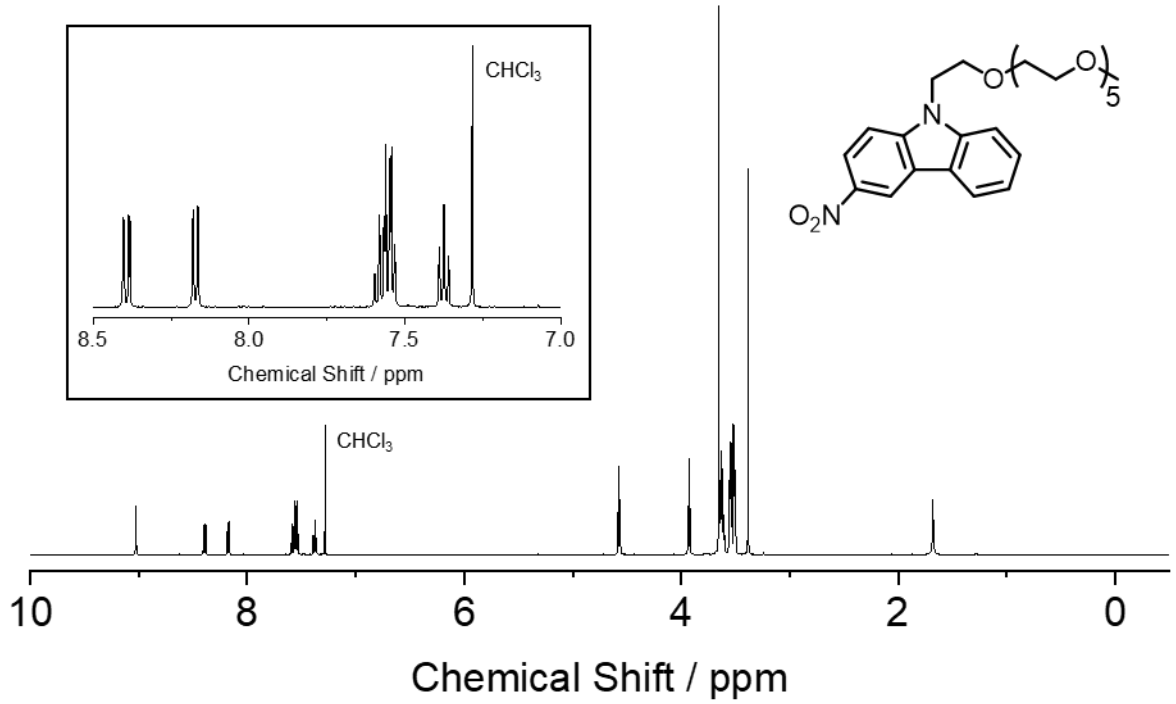


Figure S11. ^{1}H NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-3-nitro-carbazole (**3e**).

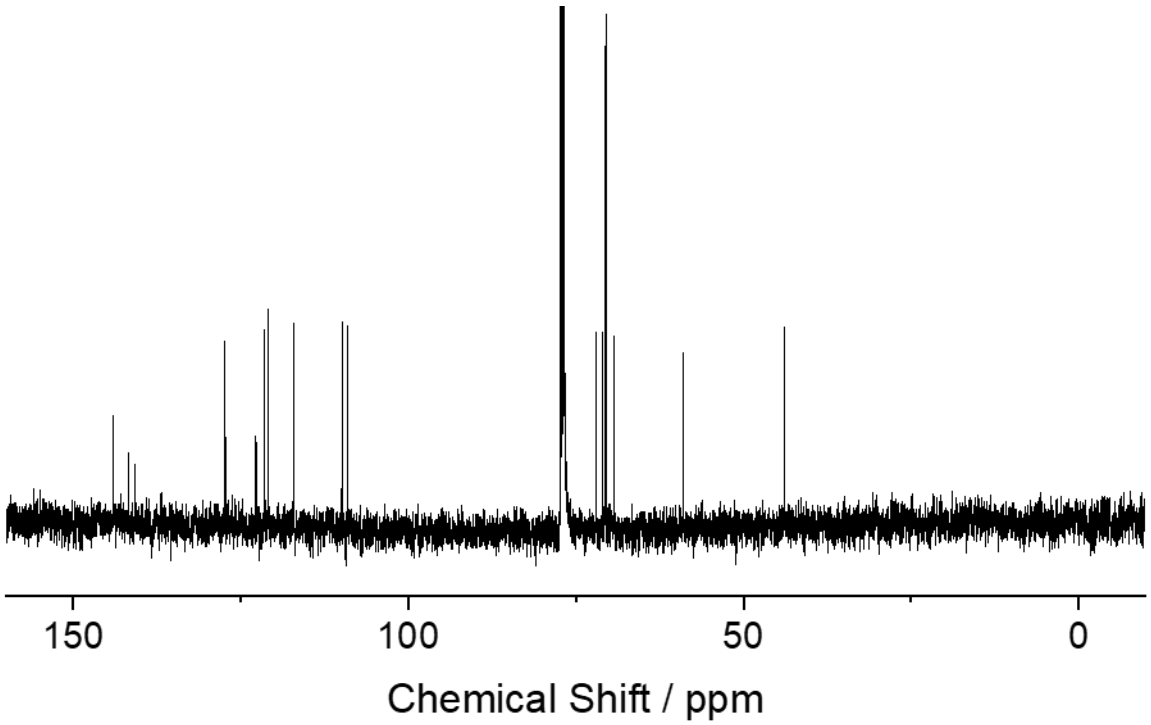


Figure S12. ^{13}C NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-3-nitro-carbazole (**3e**).

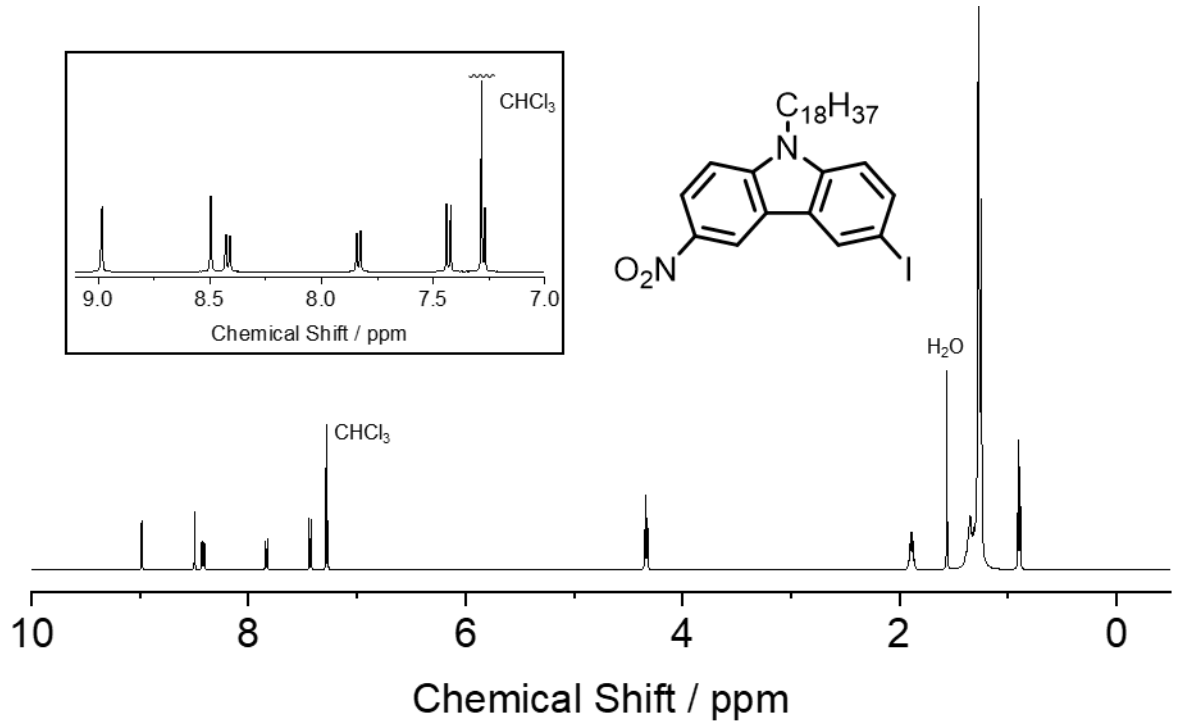


Figure S13. ^{1}H NMR spectrum of 6-iodo-3-nitro-9-octadecyl-carbazole (**4c**).

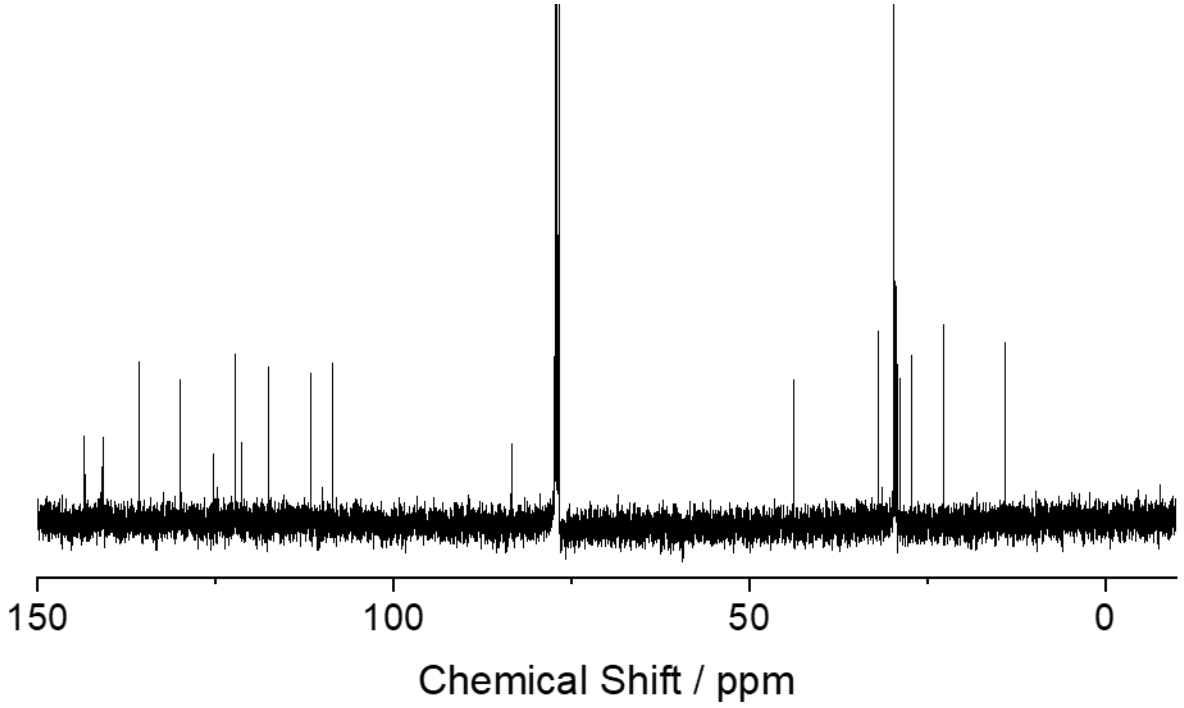


Figure S14. ^{13}C NMR spectrum of 6-iodo-3-nitro-9-octadecyl-carbazole (**4c**).

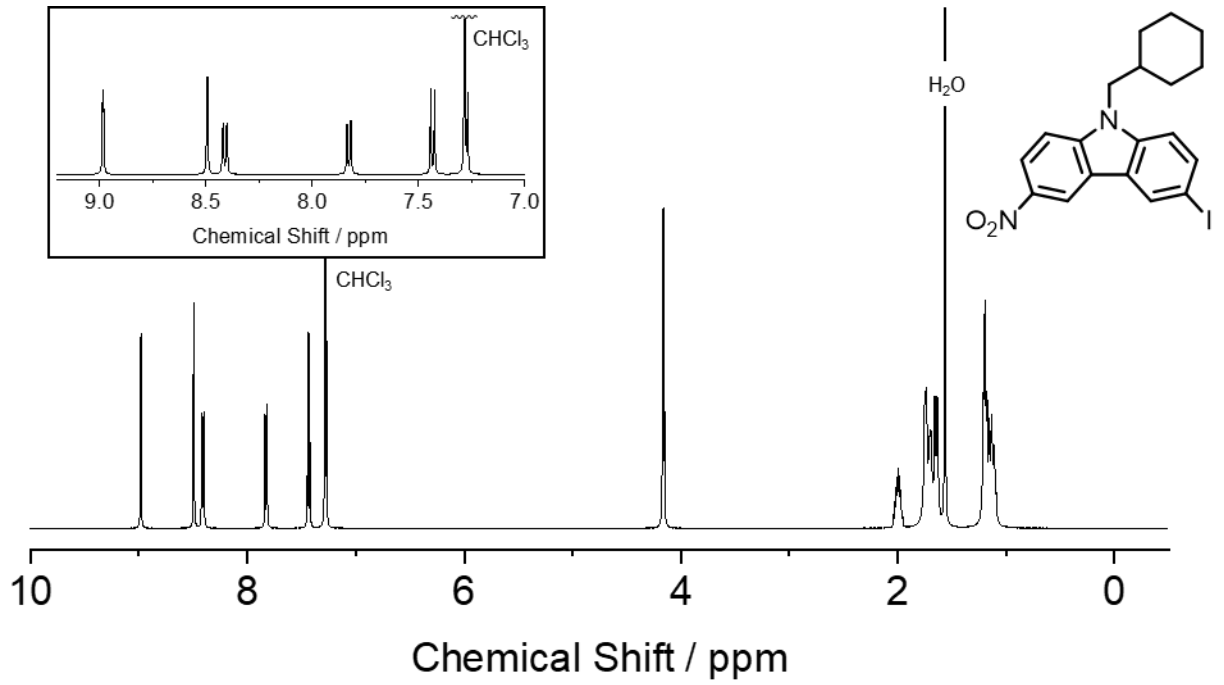


Figure S15. ^{1}H NMR spectrum of 6-iodo-9-methylcyclohexyl-3-nitro-carbazole (**4d**).

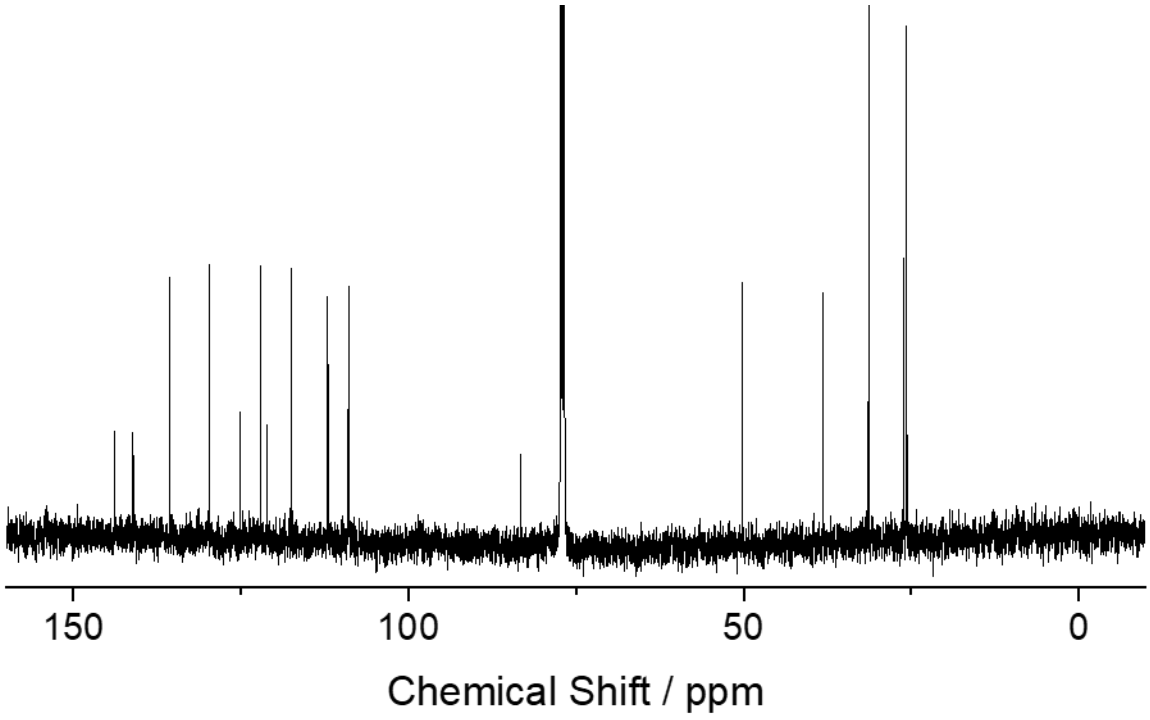


Figure S16. ^{13}C NMR spectrum of 6-iodo-9-methylcyclohexyl-3-nitro-carbazole (**4d**).

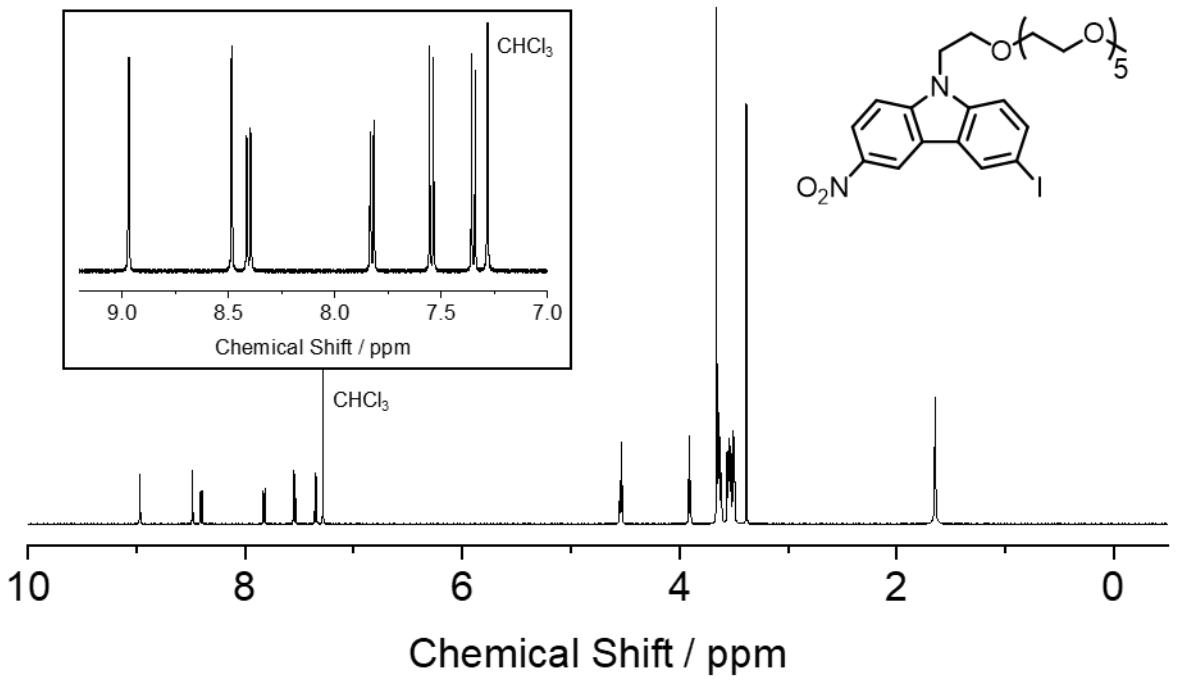


Figure S17. ^{1}H NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-iodo-3-nitro-carbazole

(**4e**).

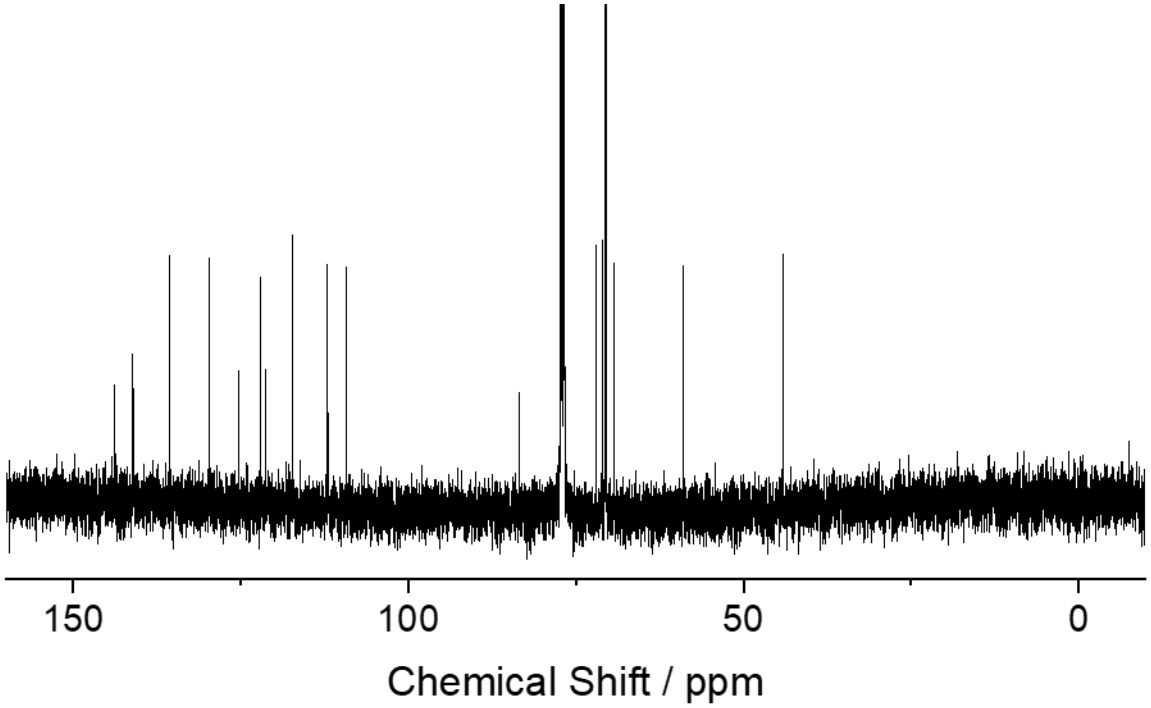


Figure S18. ^{13}C NMR spectrum of 9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-iodo-3-nitro-carbazole (**4e**).

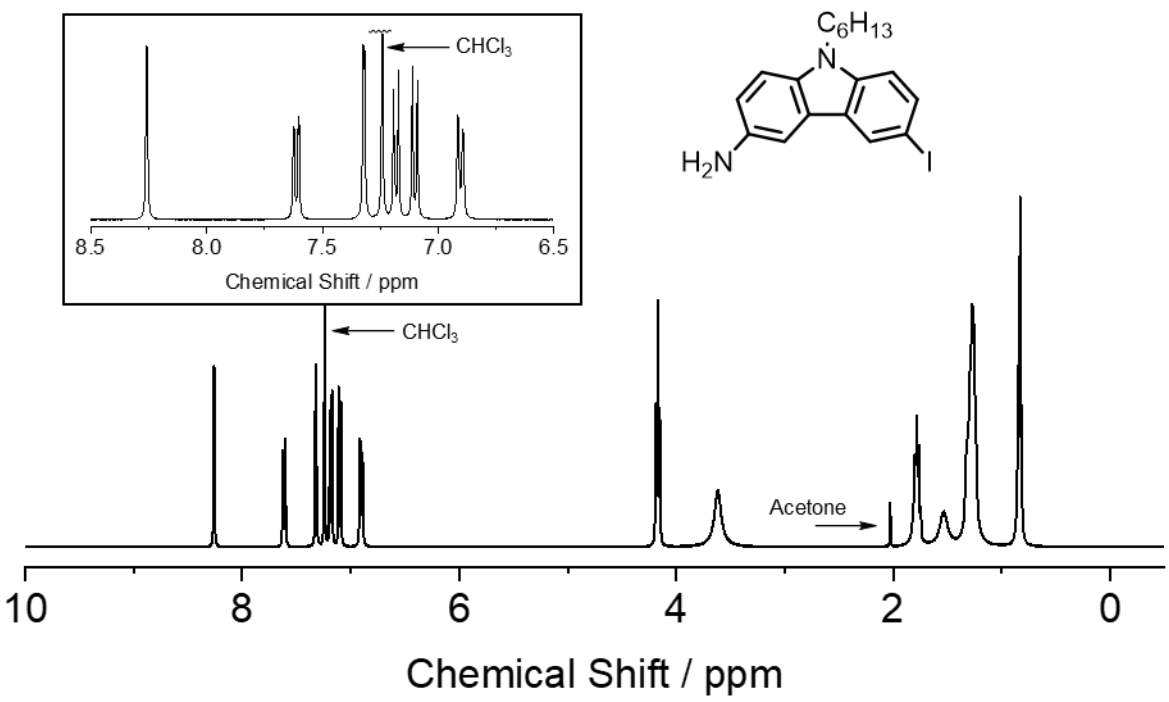


Figure S19. ^{1}H NMR spectrum of 3-amino-9-hexyl-6-iodo-carbazole (**5a**).

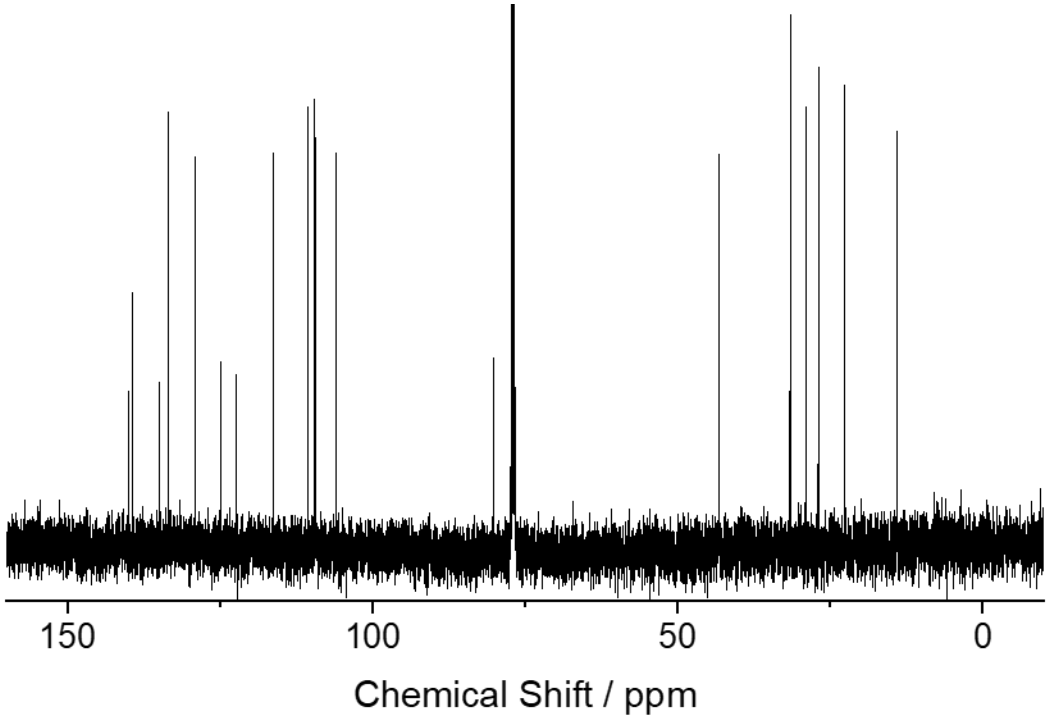


Figure S20. ^{13}C NMR spectrum of 3-amino-9-hexyl-6-iodo-carbazole (**5a**).

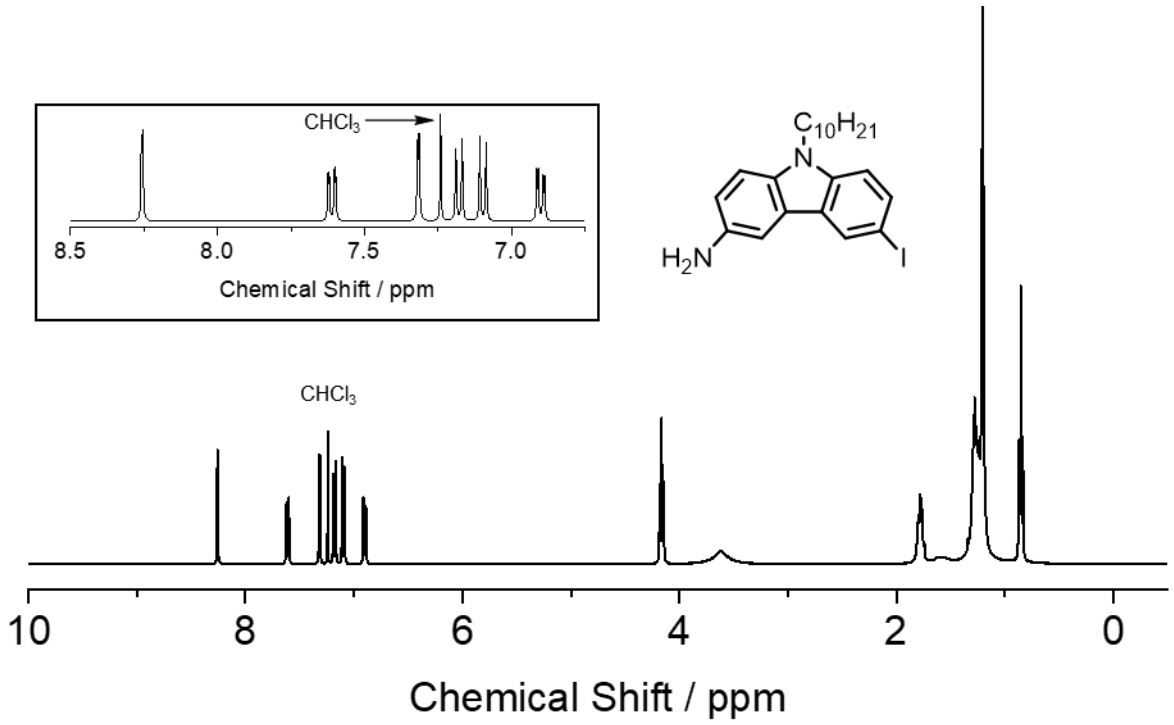


Figure S21. ^{1}H NMR spectrum of 3-amino-9-decyl-6-iodo-carbazole (**5b**).

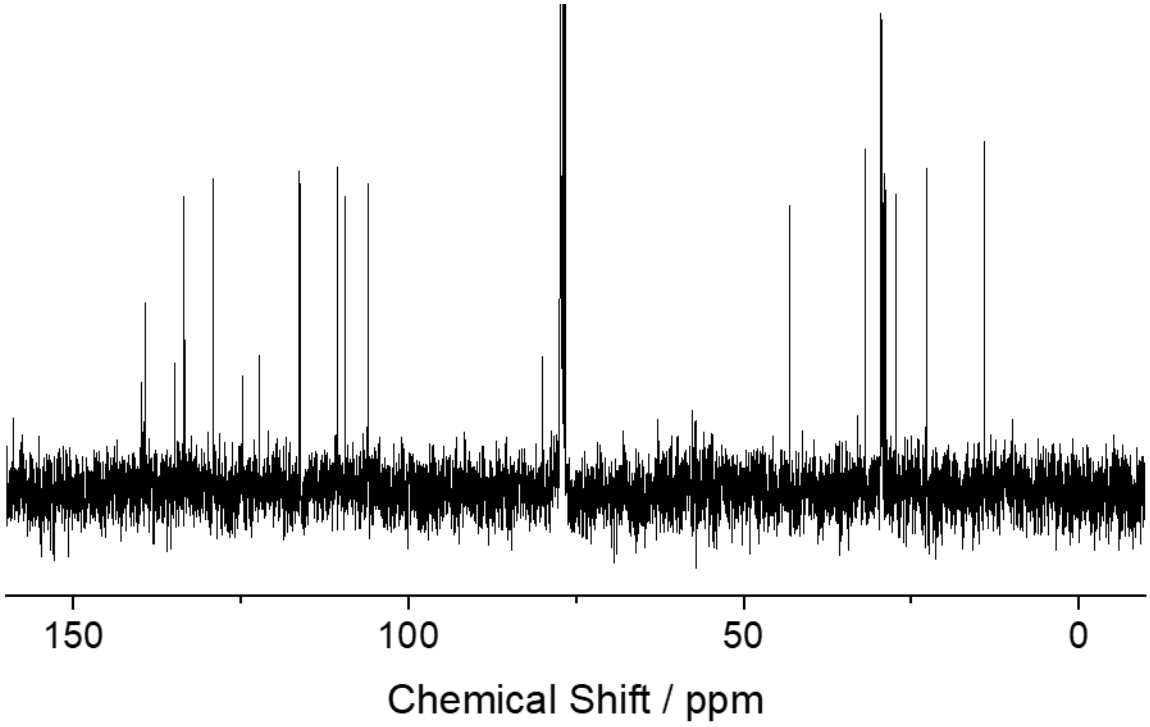


Figure S22. ^{13}C NMR spectrum of 3-amino-9-decyl-6-iodo-carbazole (**5b**).

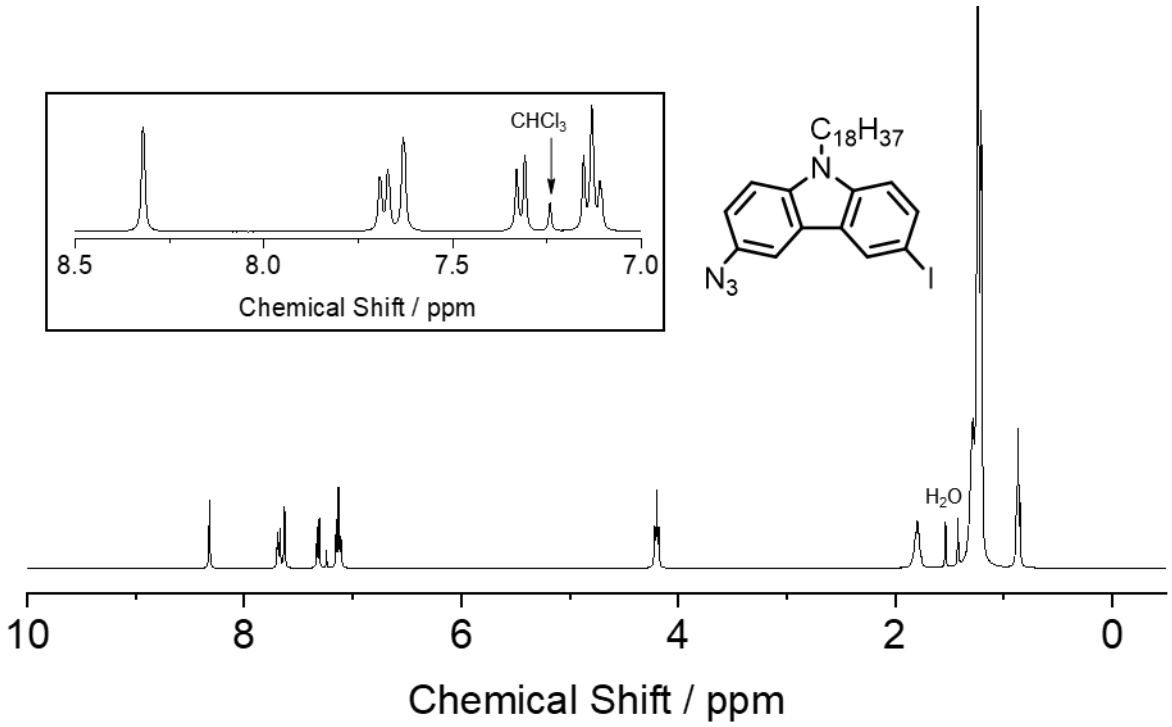


Figure S23. ^{1}H NMR spectrum of 3-azido-6-iodo-9-octadecyl-carbazole (**6c**).

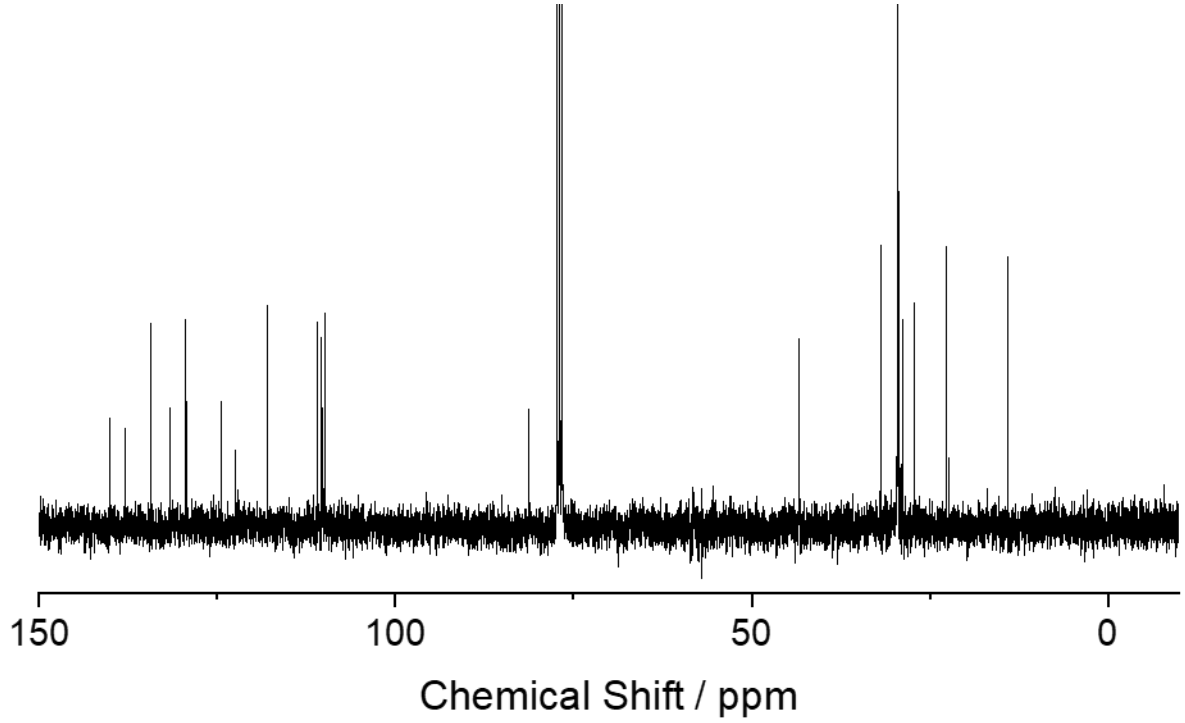


Figure S24. ^{13}C NMR spectrum of 3-azido-6-iodo-9-octadecyl-carbazole (**6c**).

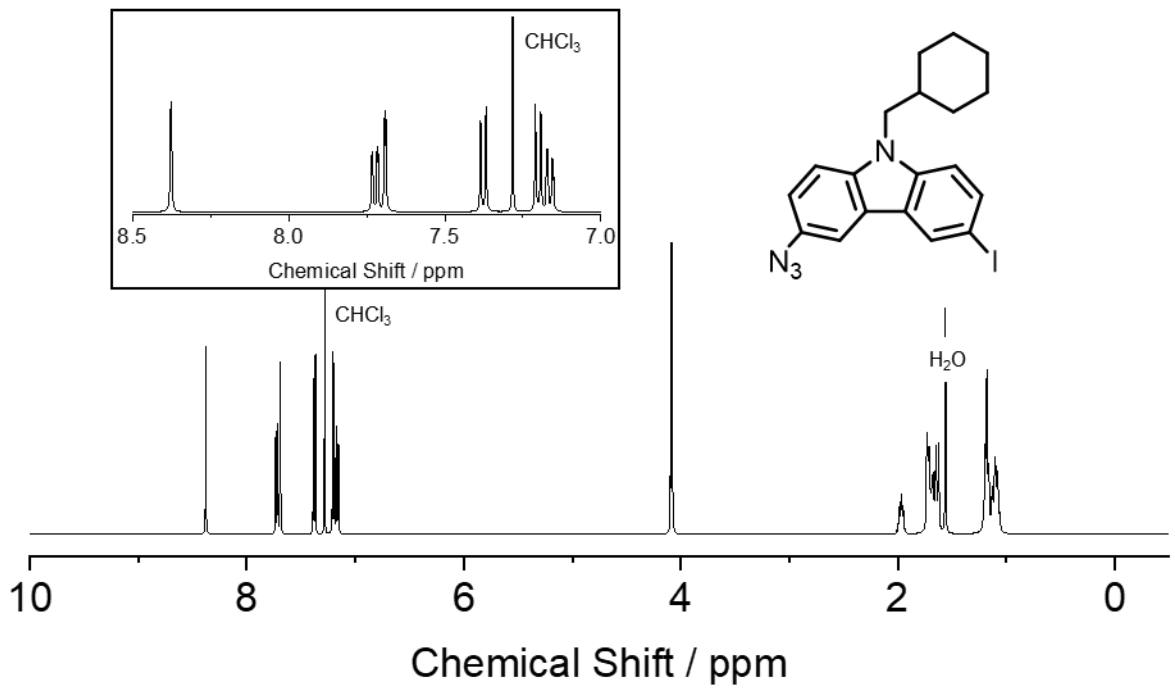


Figure S25. ^{1}H NMR spectrum of 3-azido-6-iodo-9-methylcyclohexyl-carbazole (**6d**).

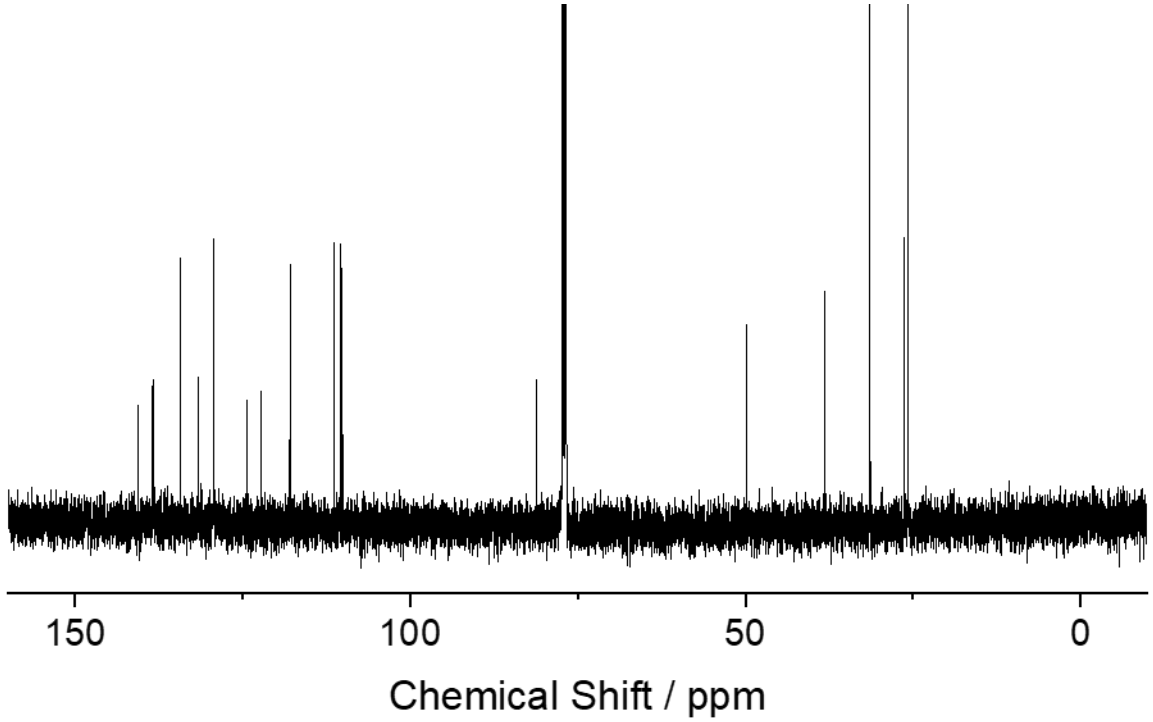


Figure S26. ^{13}C NMR spectrum of 3-azido-6-iodo-9-methylcyclohexyl-carbazole (**6d**).

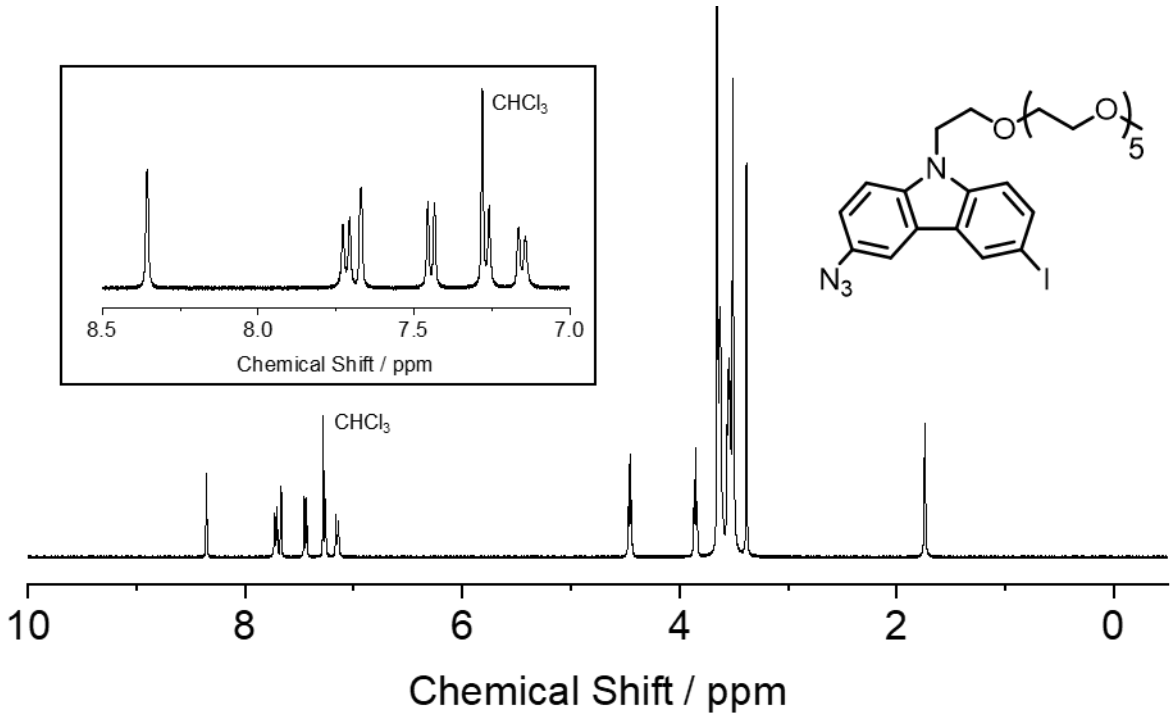


Figure S27. ^{1}H NMR spectrum of 3-azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-iodo-carbazole (**6e**).

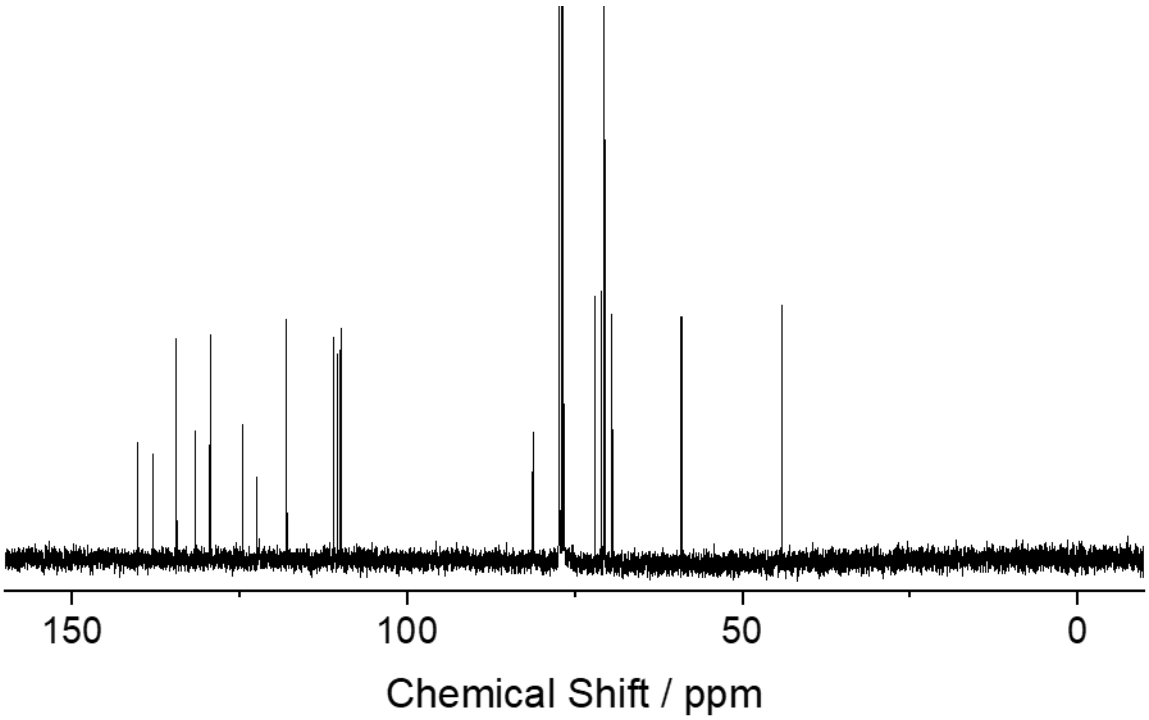


Figure S28. ^{13}C NMR spectrum of 3-azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-iodo-carbazole (**6e**).

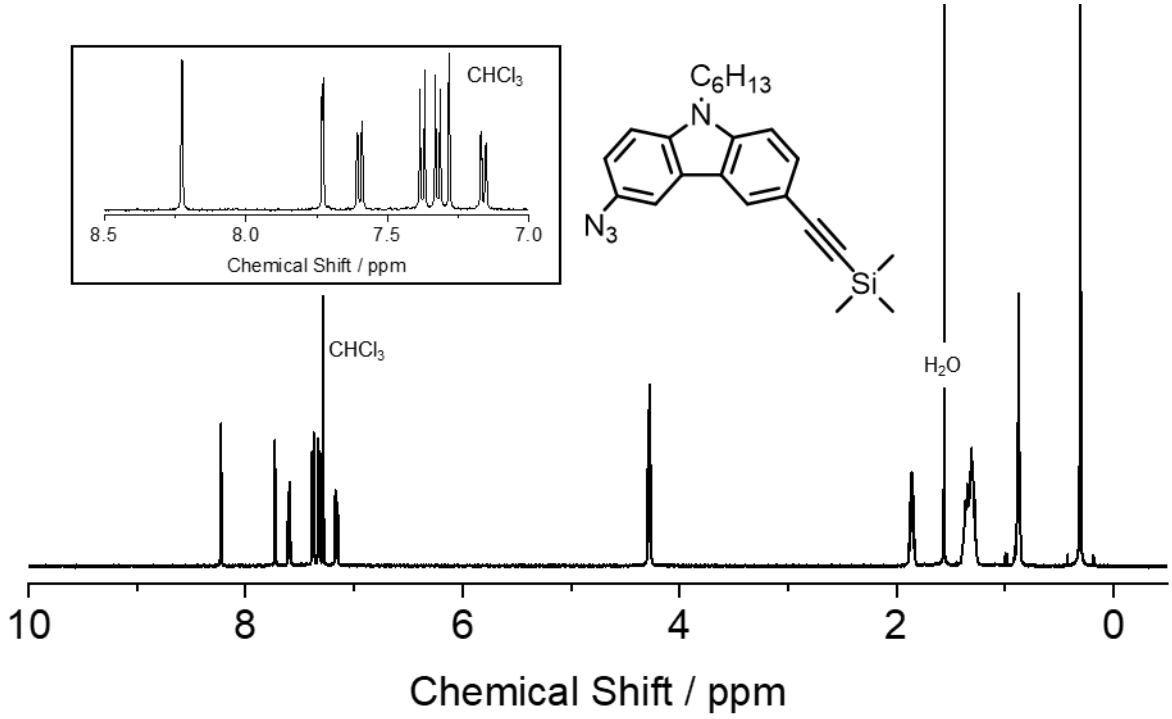


Figure S29. ^{1}H NMR spectrum of 3-azido-9-hexyl-6-((trimethylsilyl)ethynyl)-carbazole (**7a-TMS**).

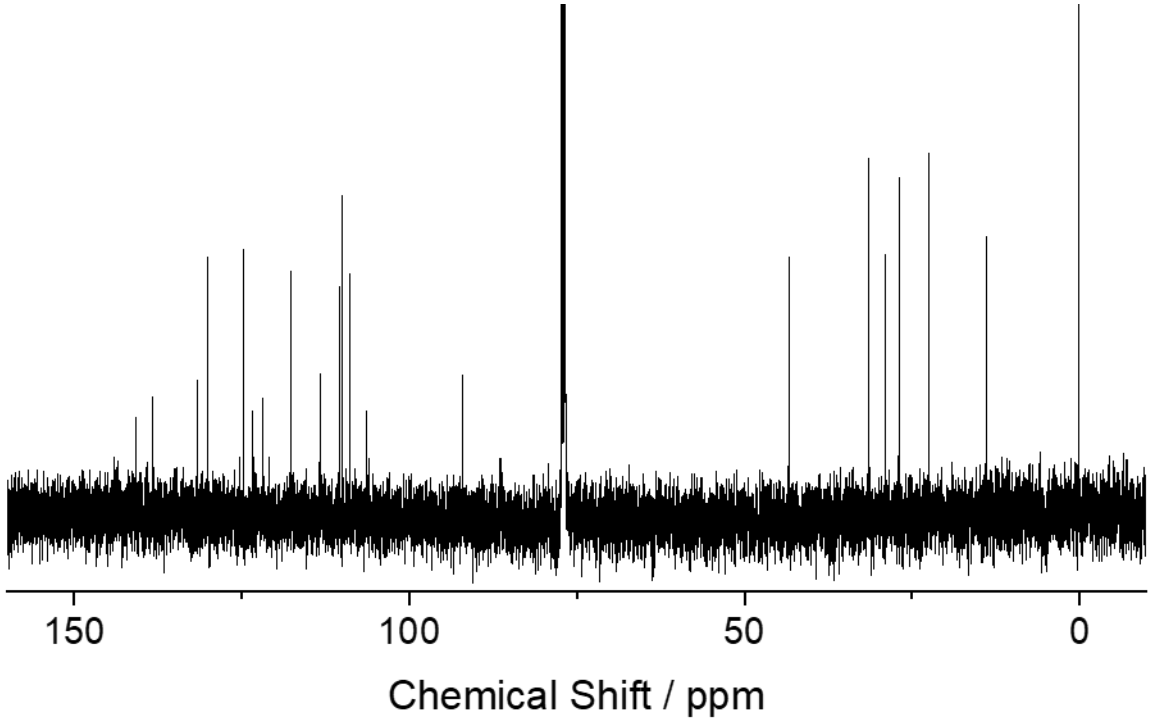


Figure S30. ^{13}C NMR spectrum of 3-azido-9-hexyl-6-((trimethylsilyl)ethynyl)-carbazole (**7a-TMS**).

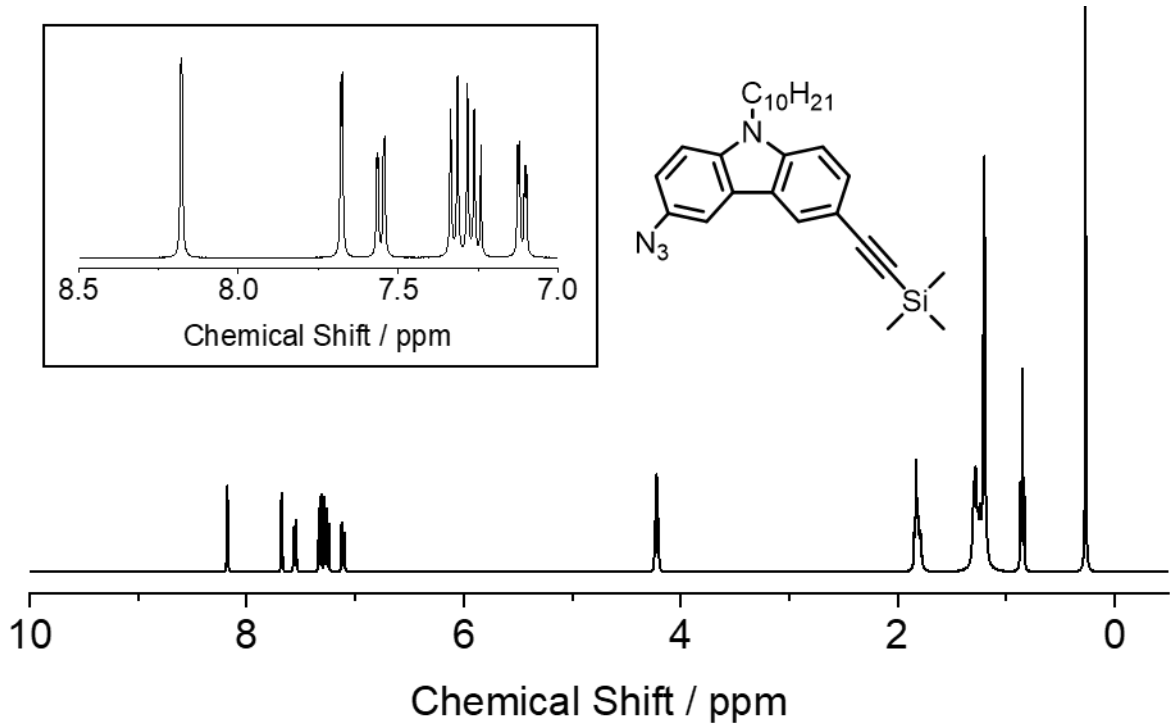


Figure S31. ^{1}H NMR spectrum of 3-azido-9-decyl-6-((trimethylsilyl)ethynyl)-carbazole (**7b-TMS**).

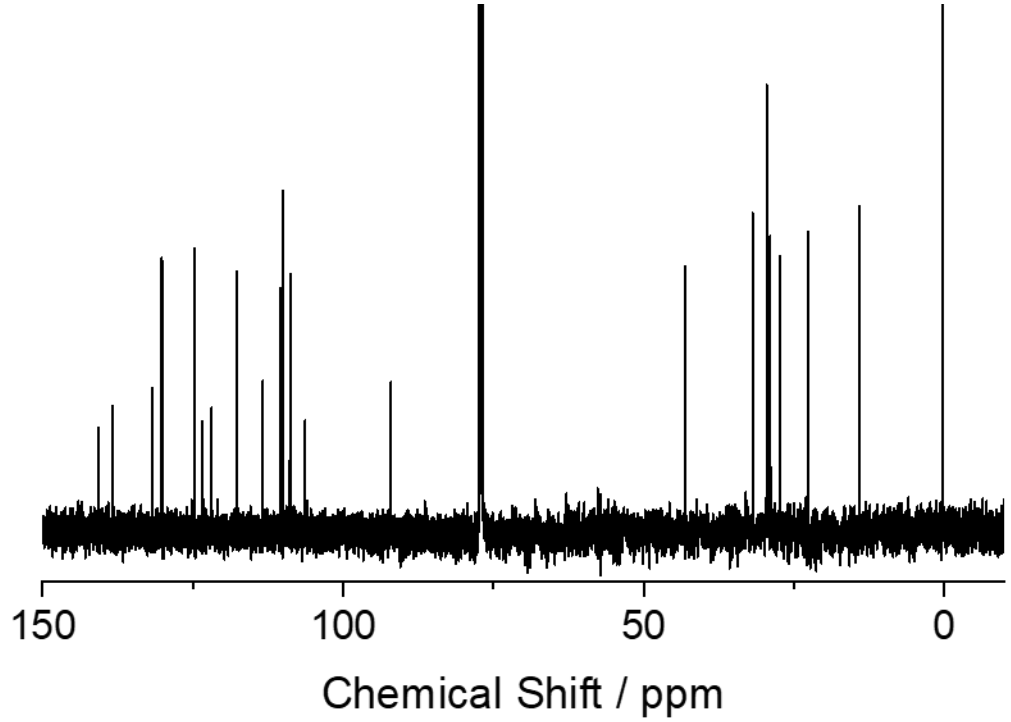


Figure S32. ^{13}C NMR spectrum of 3-azido-9-decyl-6-((trimethylsilyl)ethynyl)-carbazole (**7b-TMS**).

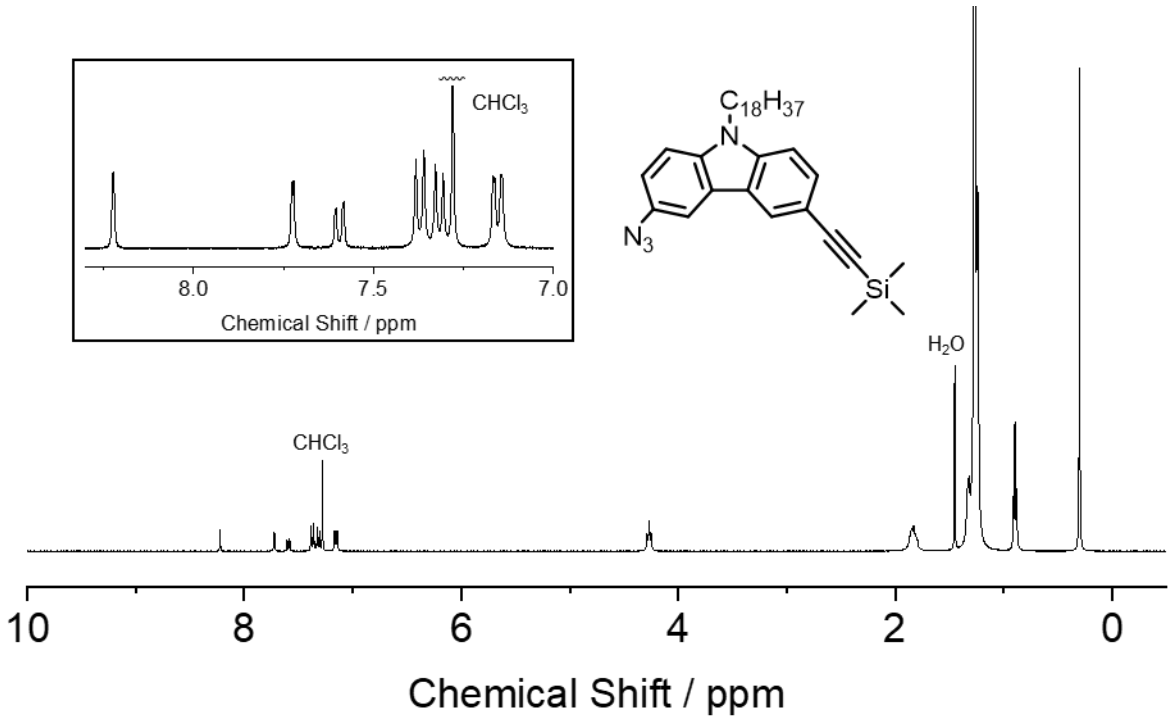


Figure S33. ^{1}H NMR spectrum of 3-azido-9-octadecyl-6-((trimethylsilyl)ethynyl)-carbazole (**7c-TMS**).

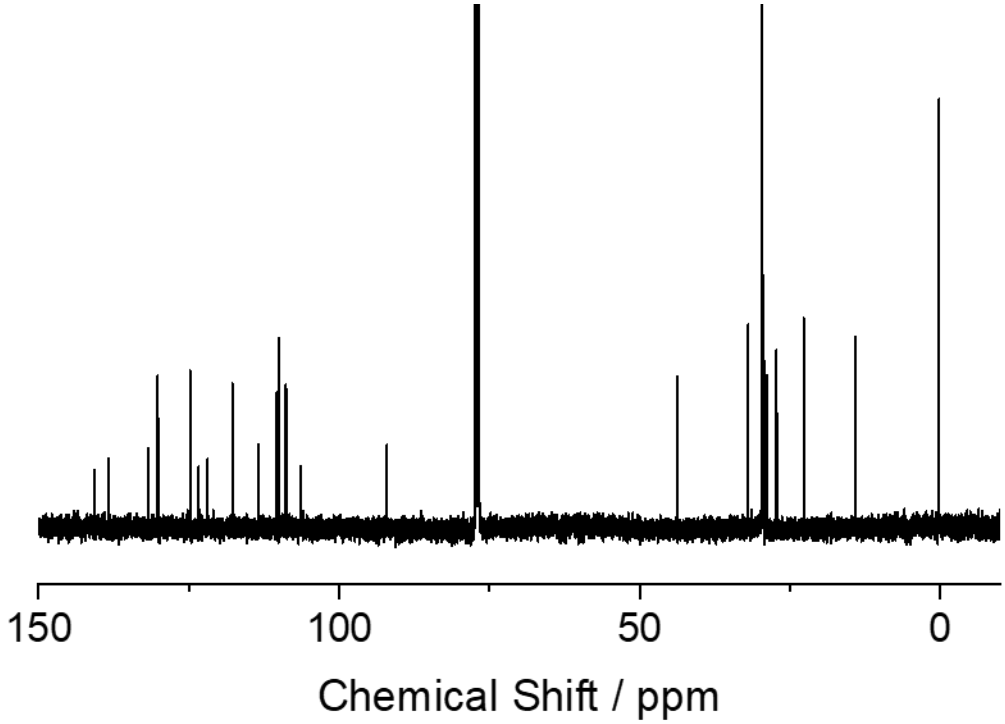


Figure S34. ^{13}C NMR spectrum of 3-azido-9-octadecyl-6-((trimethylsilyl)ethynyl)-carbazole (**7c-TMS**).

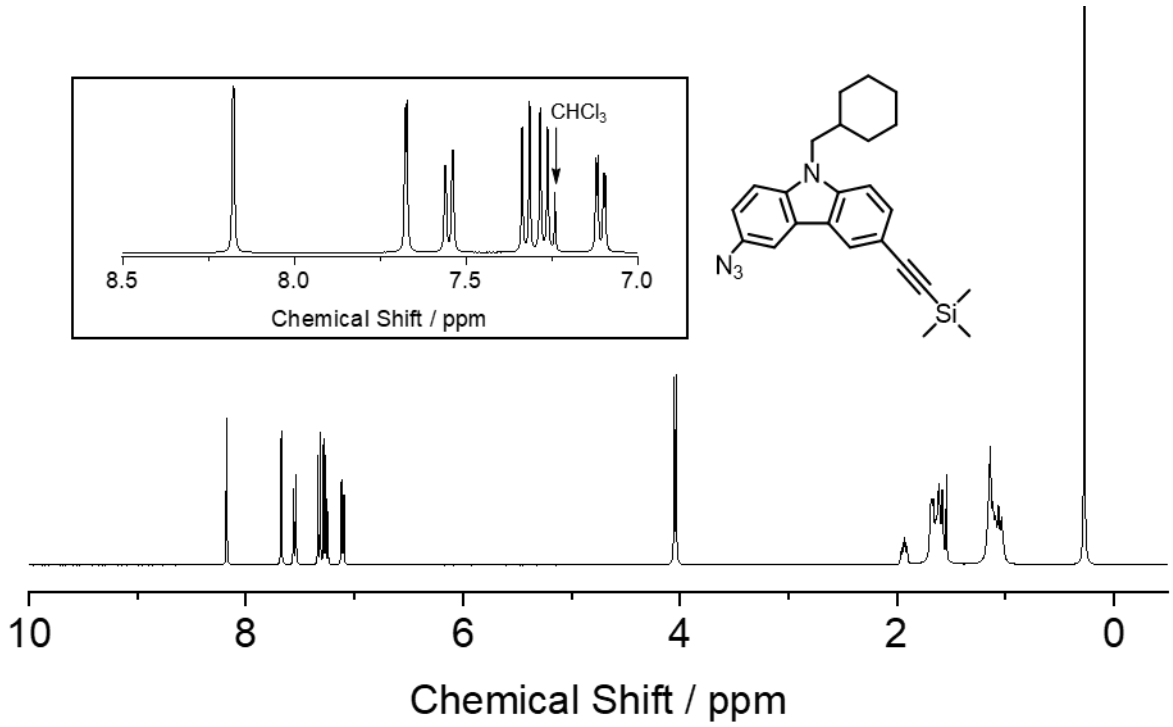


Figure S35. ^{1}H NMR spectrum of 3-azido-9-methylcyclohexyl-6-((trimethylsilyl)ethynyl)-carbazole (**7d-TMS**).

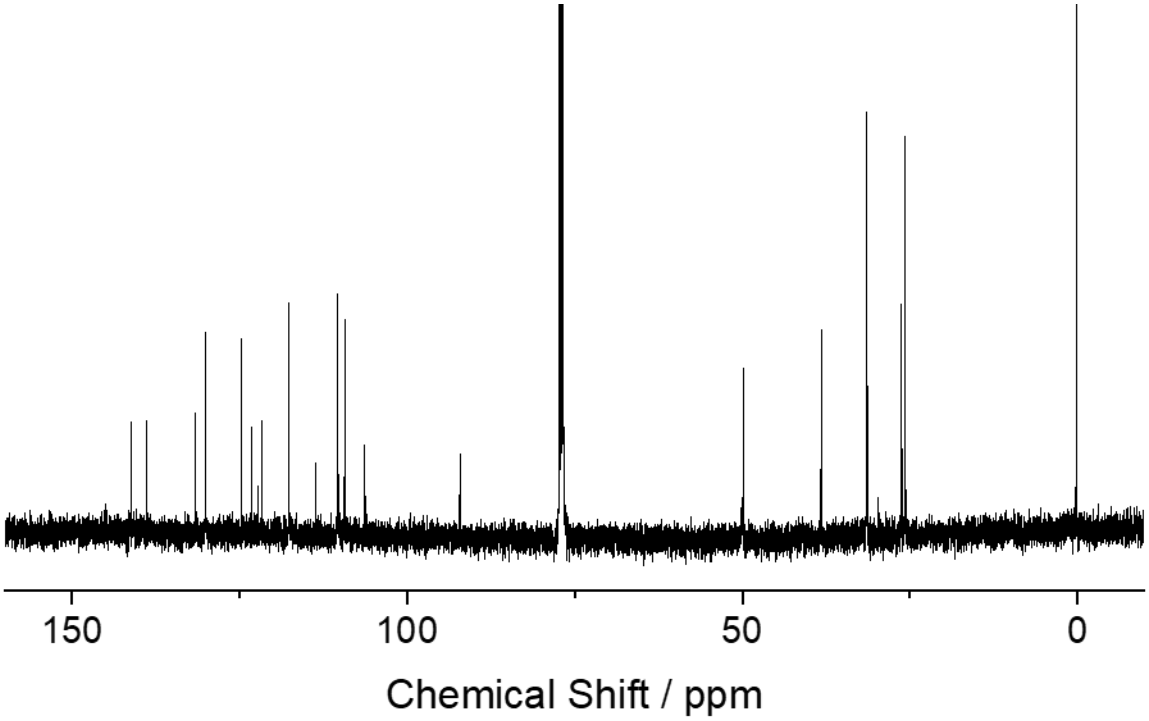


Figure S36. ^{13}C NMR spectrum of 3-azido-9-methylcyclohexyl-6-((trimethylsilyl)ethynyl)-carbazole (**7d-TMS**).

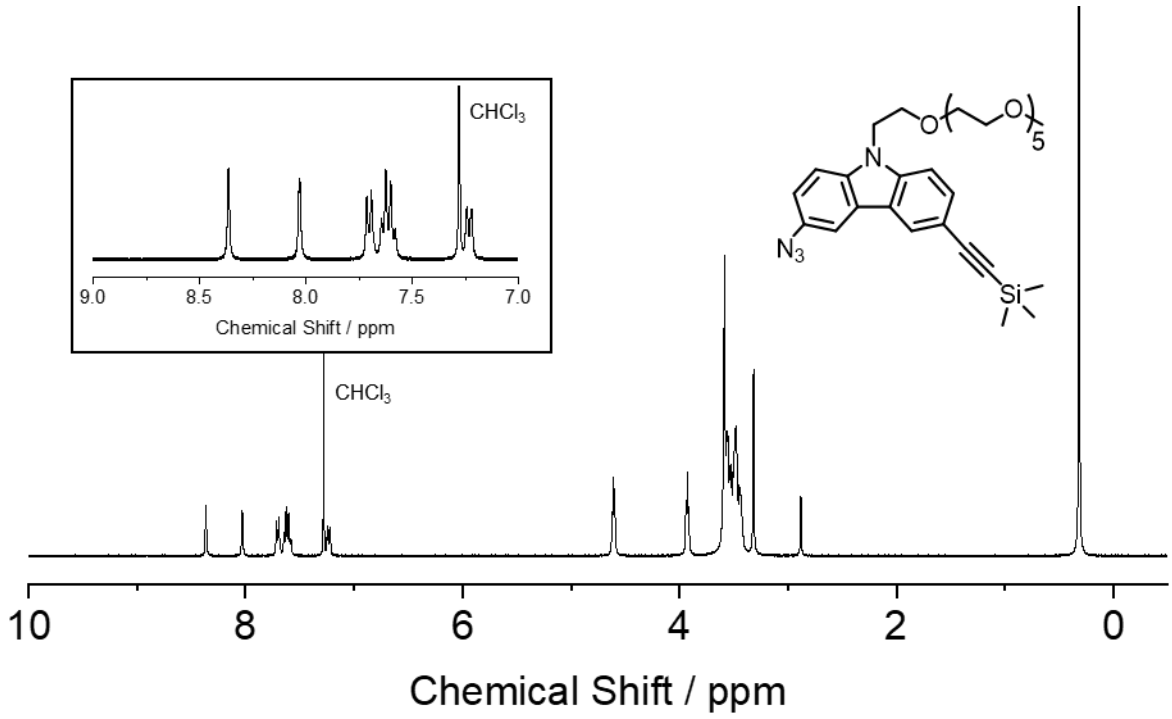


Figure S37. ^{1}H NMR spectrum of 3-azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-((trimethylsilyl)ethynyl)-carbazole (**7e-TMS**).

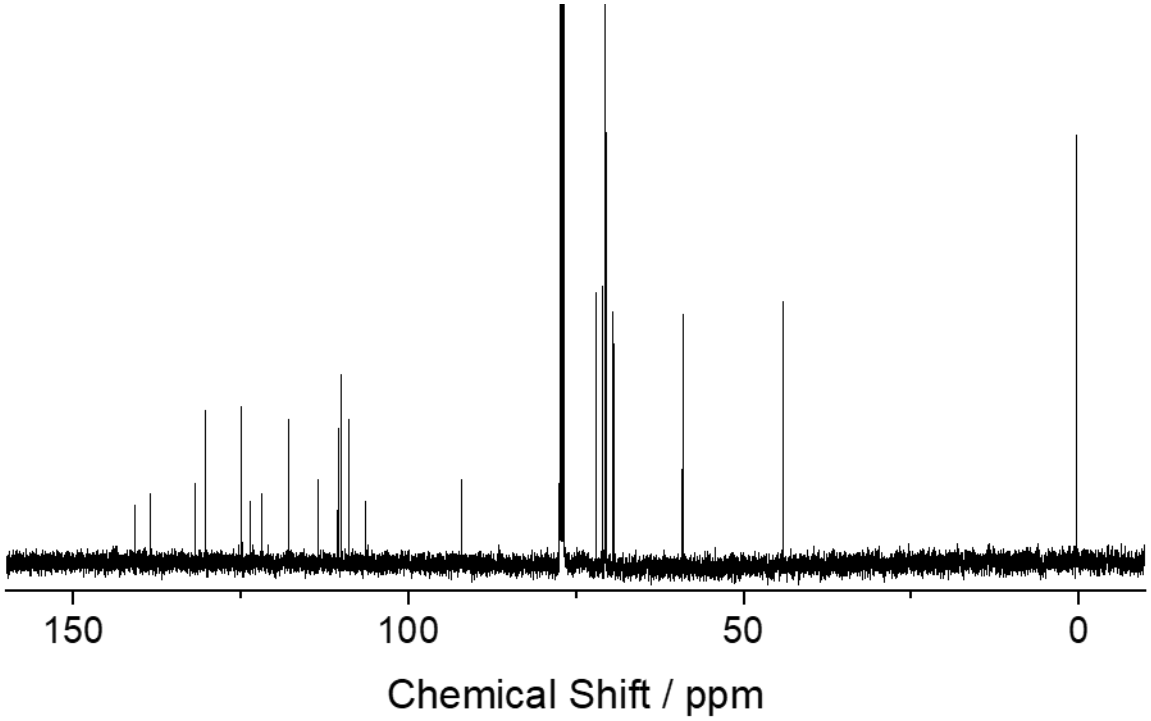


Figure S38. ^{13}C NMR spectrum of 3-azido-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-((trimethylsilyl)ethynyl)-carbazole (**7e-TMS**).

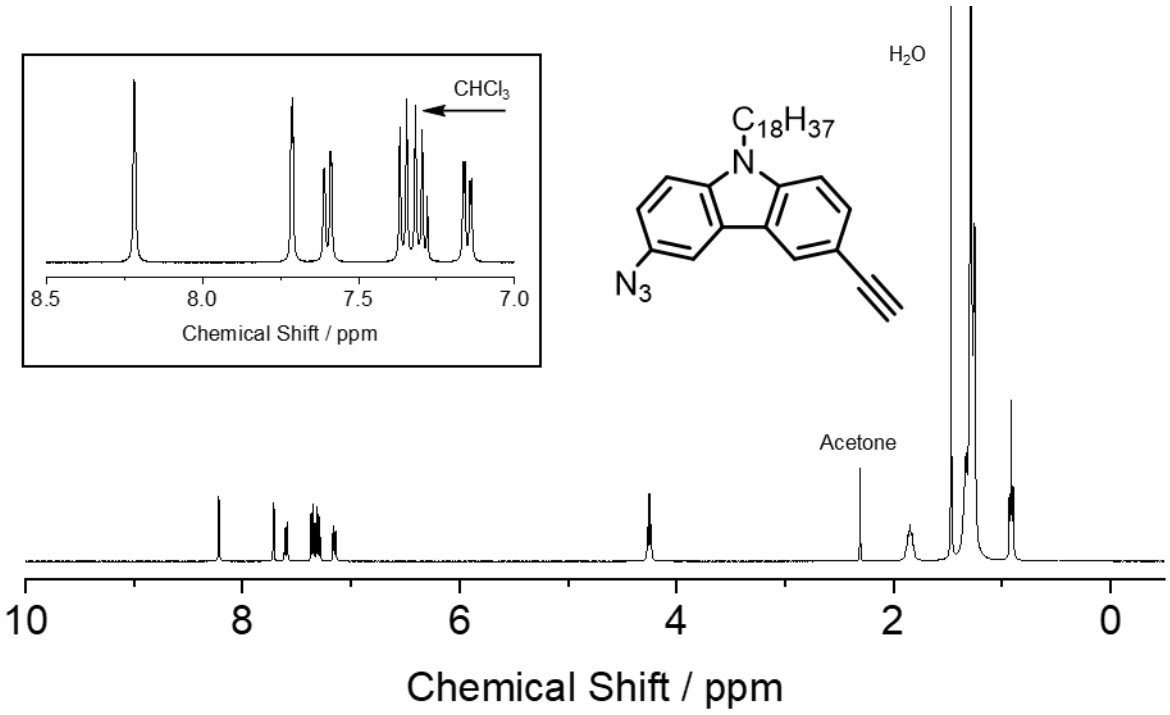


Figure S39. ^{1}H NMR spectrum of 3-azido-9-octadecyl-6-ethynyl-carbazole (**7c**).

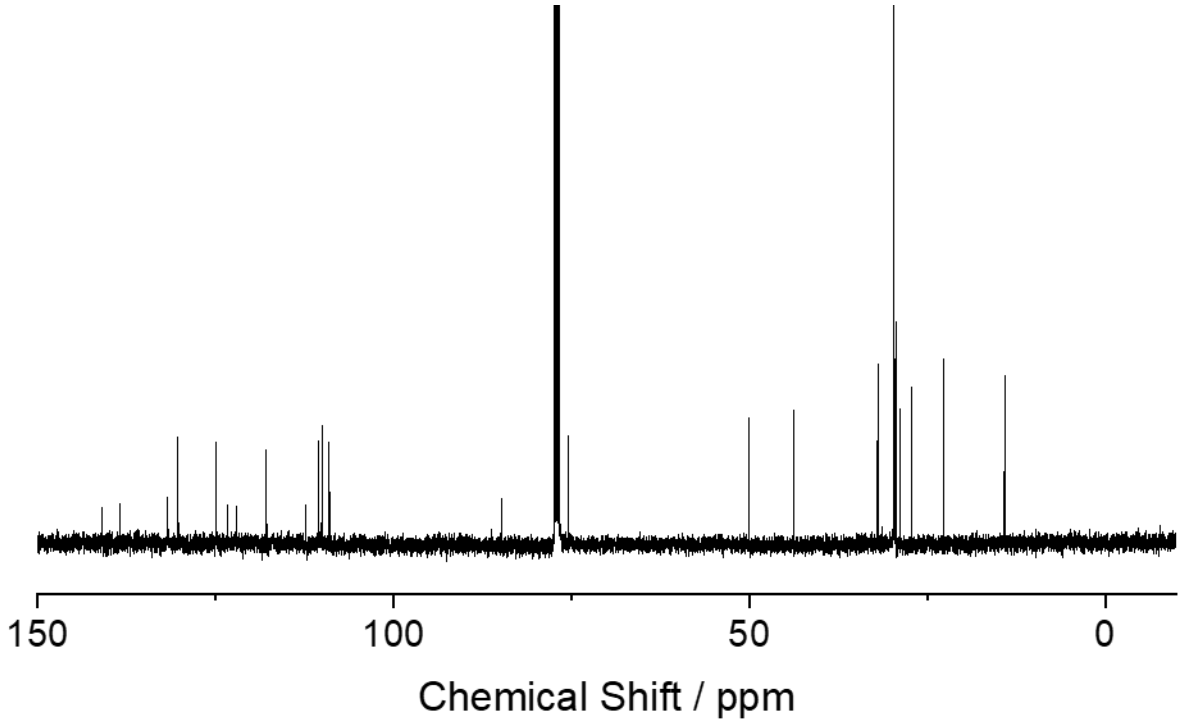


Figure S40. ^{13}C NMR spectrum of 3-azido-9-octadecyl-6-ethynyl-carbazole (**7c**).

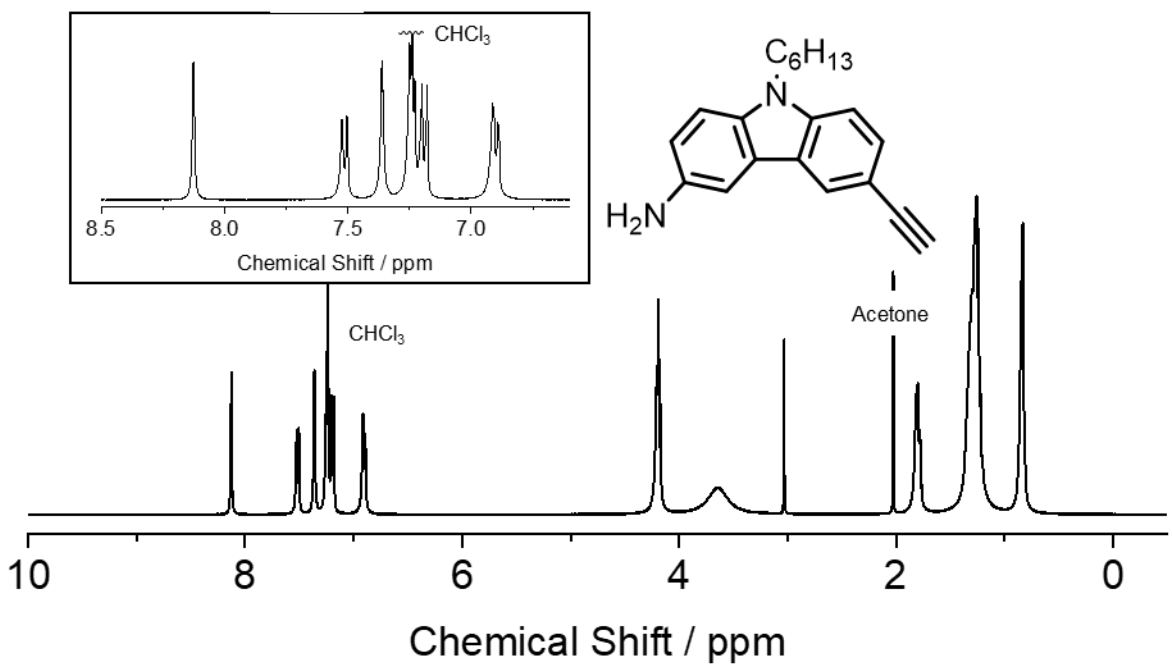


Figure S41. ^{1}H NMR spectrum of 3-amino-6-ethynyl-9-hexyl-carbazole (**8a**).

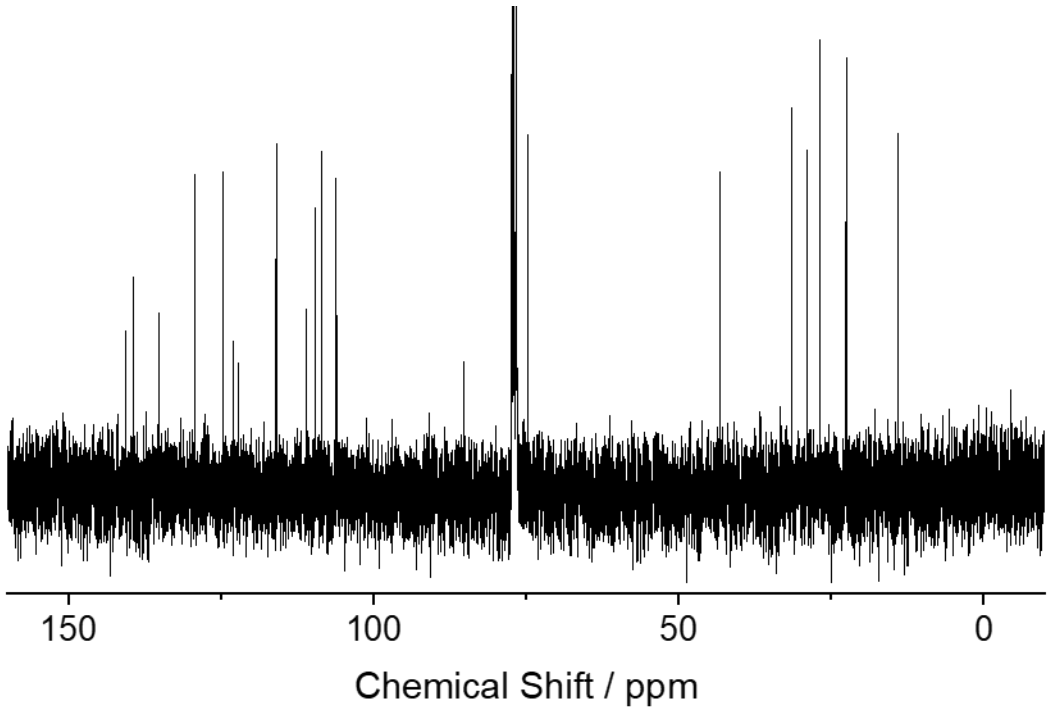


Figure S42. ^{13}C NMR spectrum of 3-amino-6-ethynyl-9-hexyl-carbazole (**8a**).

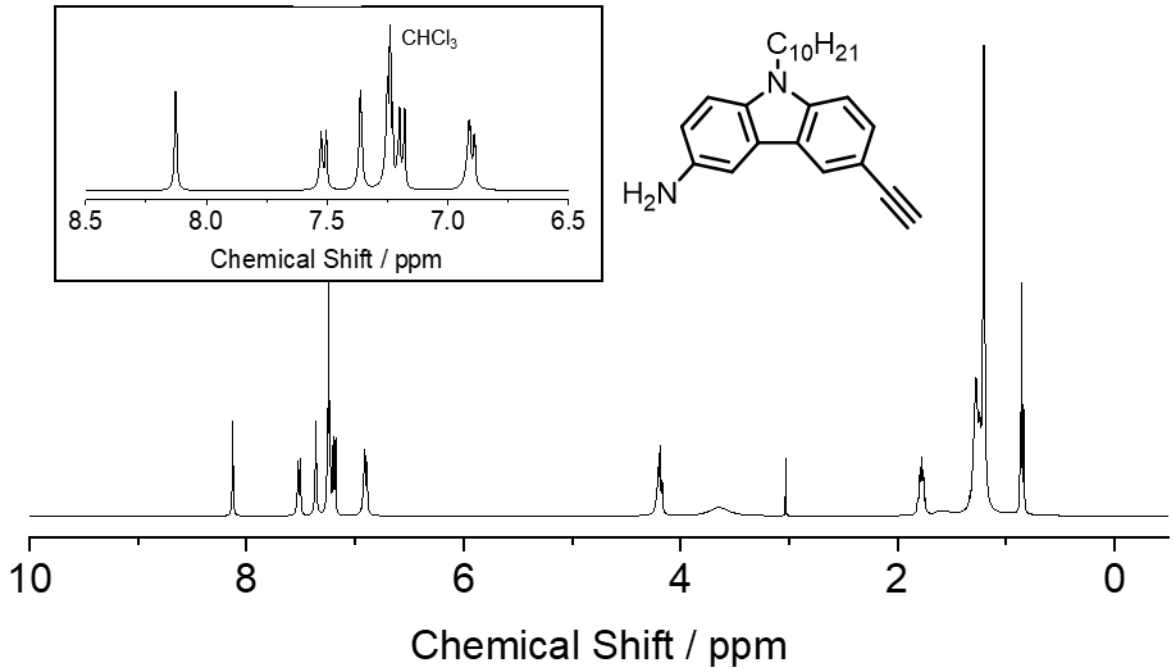


Figure S43. ^{1}H NMR spectrum of 3-amino-9-decyl-6-ethynyl-carbazole (**8b**).

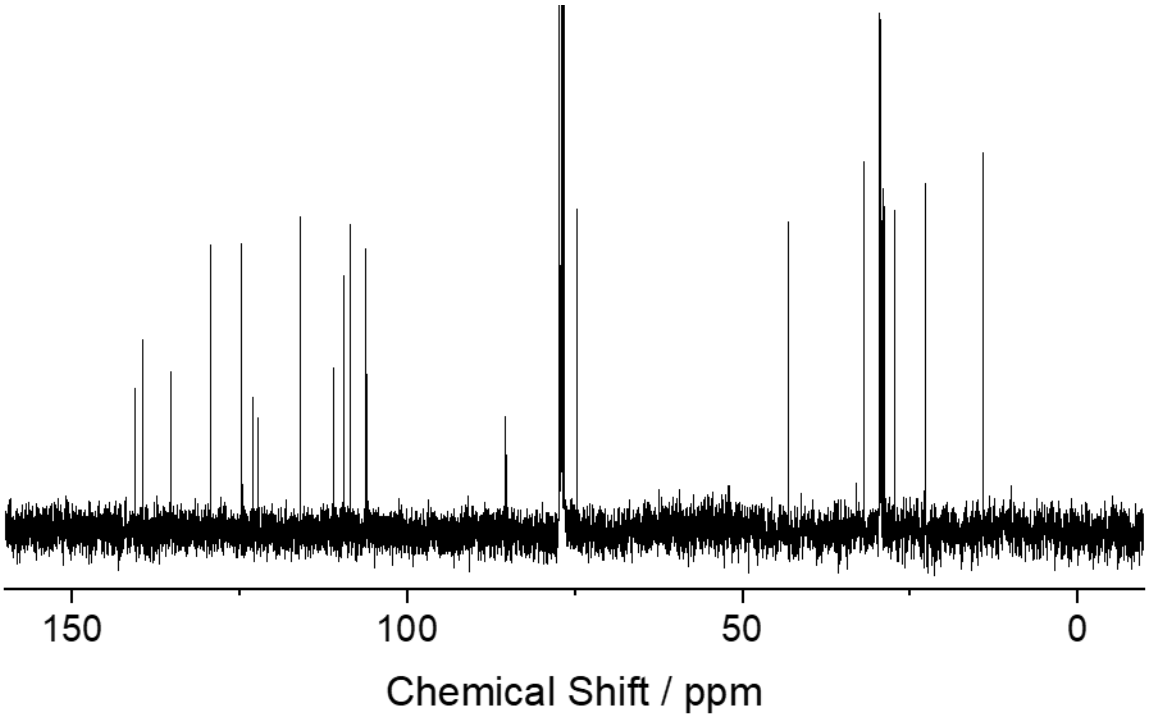
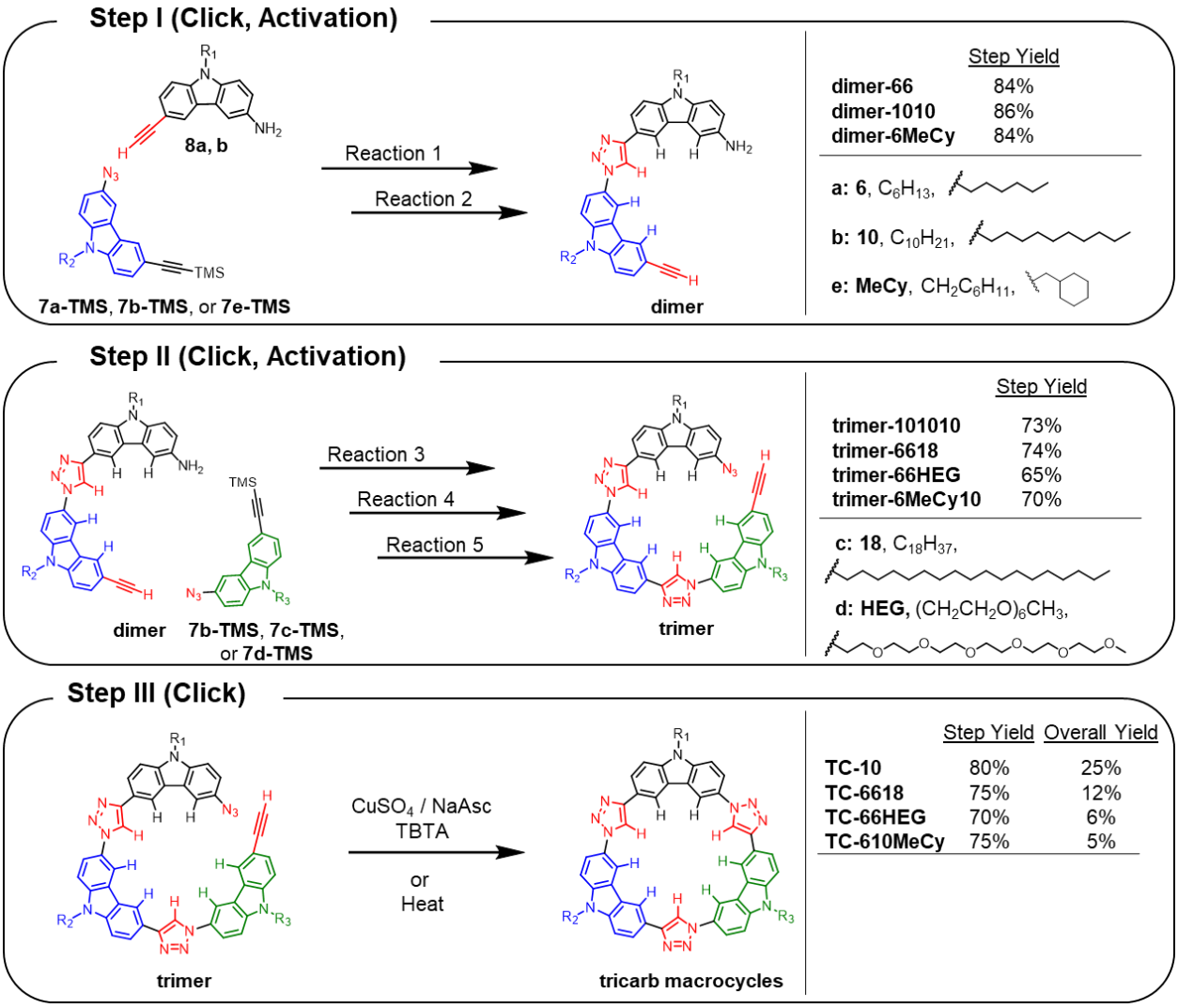


Figure S44. ^{13}C NMR spectrum of 3-amino-9-decyl-6-ethynyl-carbazole (**8b**).

S4. General Synthesis and Characterization of Crescents



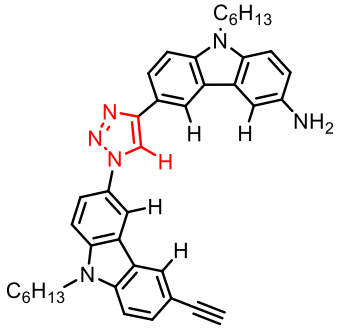
Scheme 3. General step-wise synthesis of broken symmetry tricarb macrocycles.

Step I (Reactions 1 and 2): Formation of the amino-alkynyl-crescent dimer – Amino-carbazole **8** and azido-carbazole **7-TMS** were dissolved in a 2:1:1 mixture of THF, ethanol, and water. The solution was then degassed with argon for 15 minutes. A solution of $CuSO_4 \cdot 5H_2O$, sodium ascorbate and TBTA in a 2:1:1 mixture of THF, ethanol, and water was then added to the degassed carbazole solution. The reaction mixture was heated to 60 °C and stirred for 6 hours, then cooled to room temperature. The reaction was quenched by the addition of an aqueous solution of NH_4Cl (1M) and the resulting mixture was extracted with three portions of $CHCl_3$. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting crescent dimer intermediate was then dissolved in a 2:1 mixture of THF and MeOH to which a saturated solution of K_2CO_3 in MeOH was added. The reaction stirred for 1 hour and was quenched with an aqueous NH_4Cl solution (1 M). The resulting mixture was extracted with three portions of

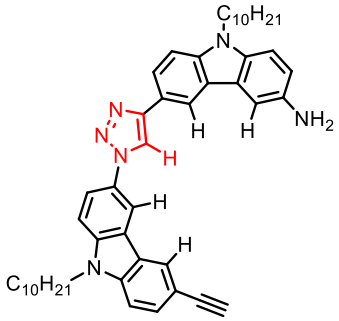
$CHCl_3$, the combined organic layers were dried with $MgSO_4$, filtered, and then concentrated in vacuo. The resulting amino-crescent **dimer** was purified by column chromatography.

Step II (Reaction 3): Formation of the amino-trimethylsilylalkynyl-crescent trimer – Amino-crescent **dimer** and azido-carbazole **7-TMS** were dissolved in a 2:1:1 mixture of THF, ethanol, and water. The solution was degassed with argon for 15 minutes. A solution of $CuSO_4 \cdot 5H_2O$, sodium ascorbate and TBTA in a 2:1:1 mixture of THF, ethanol, and water was added to the degassed carbazole solution. The reaction mixture was heated to 60 °C and stirred for 6 hours, cooled to room temperature. The reaction was quenched by the addition of an aqueous solution of NH_4Cl (1M) and the resulting mixture was extracted with three portions of $CHCl_3$. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting amino-crescent **trimer** was purified by column chromatography.

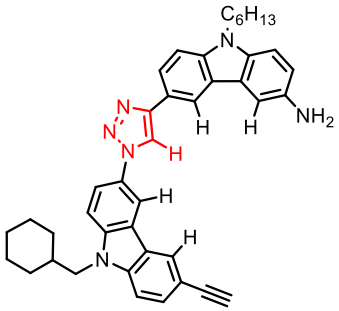
Step II (Reaction 4 and 5): Formation of the azido-alkynyl crescent trimer – Amino-crescent **trimer** and *p*-toluenesulfonic acid monohydrate were dissolved in THF and cooled to 0 °C using an ice bath. Upon cooling, the solution forms a dark brown slurry. A solution of $NaNO_2$ in water was added dropwise and the resulting mixture was stirred for 30 minutes. A solution of NaN_3 in water was added drop-wise, followed by stirring for an additional 30 minutes at 0°C. The mixture was warmed to room temperature and stirred for an additional hour. The mixture was basified with an aqueous NaOH solution (1 M) and extracted with three portions of ethyl acetate. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting crescent trimer intermediate was then dissolved in a 2:1 mixture of THF and MeOH to which a saturated solution of K_2CO_3 in MeOH was added. The reaction stirred for 1 hour and was quenched with an aqueous NH_4Cl solution (1 M). The resulting mixture was extracted with three portions of $CHCl_3$, the combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting crescent **trimer** was purified by column chromatography.



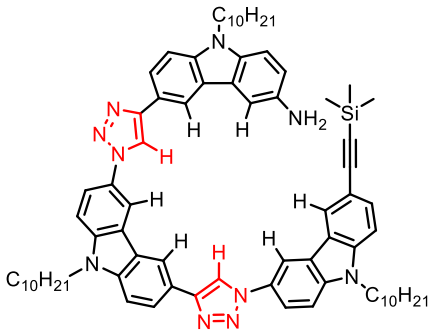
3-Amino-6-(1-(6-ethynyl-9-hexyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (dimer-66) – Dimer-66 was synthesized following the general procedure for the formation of amino-alkynyl-crescent dimers using amino-carbazole **8a** (1.46 g, 5 mmol, 1 equiv.), azido-carbazole **7a-TMS** (2.14 g, 5.5 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (125 mg, 0.5 mmol, 0.1 equiv.), TBTA (265 mg, 0.5 mmol, 0.1 equiv.), and sodium ascorbate (396 mg, 1 mmol, 0.2 equiv.). Crude **dimer-66** was purified by column chromatography on silica gel using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (2.55 g, 4.2 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.45 (s, 1H), 8.33 (s, 1H), 8.30 (s, 1H), 8.00 (d, J = 6.7 Hz, 1H), 7.96 (d, J = 6.8 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.44 (d, J = 6.8 Hz, 1H), 7.39 (d, J = 6.6 Hz, 1H), 7.26 (d, J = 6.8 Hz, peak partially overlaps with residual solvent peak), 6.97 (d, J = 6.8 Hz, 1H), 4.36 (t, J = 5.2 Hz, 2H), 4.29 (t, J = 5.5 Hz, 2H), 1.99 – 1.82 (m, 4H), 1.81 – 1.03 (m, 12H) 0.89 (t, J = 5.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.58, 139.9, 134.96, 133.49, 130.62, 129.76, 129.12, 125.05, 124.9, 122.85, 122.32, 122.22, 119.43, 119.34, 116.22, 113.3, 113.01, 110.62, 109.81, 109.51, 109.28, 106.01, 84.51, 80.08, 75.8, 43.54, 43.28, 31.93, 31.60, 29.05, 28.98, 27.28, 27.00, 22.69, 22.57, 14.12, 14.02. HRMS (EI) calcd for $C_{40}H_{42}N_6$+H: 607.3544 $[M+H]^+$; found: 607.3572.



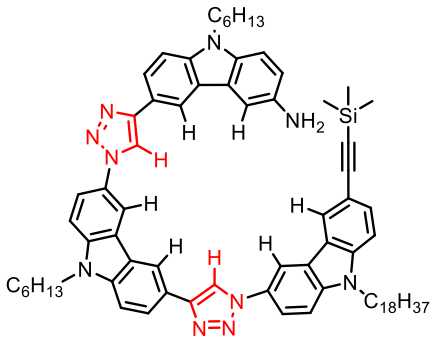
3-Amino-6-(1-(6-ethynyl-9-decyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-decyl-carbazole (dimer-1010) – Dimer-1010 was synthesized following the general method for the synthesis of amino-alkynyl-crescent dimers by using amino-carbazole **8b** (1.74 g, 5 mmol, 1 equiv.), azido-carbazole **7b-TMS** (2.44 g, 5.5 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (125 mg, 0.5 mmol, 0.1 equiv.), TBTA (265 mg, 0.5 mmol, 0.1 equiv.), and sodium ascorbate (396 mg, 1 mmol, 0.2 equiv.). The crude **dimer-1010** was purified by column chromatography on silica gel using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (3.09 g, 4.3 mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 1.6 Hz, 1H), 8.36 (d, J = 2.1 Hz, 1H), 8.27 (d, J = 1.4 Hz, 1H), 8.22 (s, 1H), 7.96 (dd, J = 8.4, 1.7 Hz, 1H), 7.86 (dd, J = 8.7, 2.1 Hz, 1H), 7.63 (dd, J = 8.5, 1.5 Hz, 1H), 7.47 (d, J = 2.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.35 (dd, J = 13.5, 8.5 Hz, 2H), 7.20 (d, J = 8.6 Hz, 1H), 6.93 (dd, J = 8.5, 2.3 Hz, 1H), 4.21 (dt, J = 20.2, 7.3 Hz, 4H), 3.66 (s, 2H), 3.13 (s, 1H), 1.95 – 1.75 (m, 4H), 1.47 – 1.16 (m, 28H), 0.90 (t, J = 5.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.01, 140.48, 139.88, 134.90, 133.42, 130.59, 129.66, 129.07, 125.00, 124.81, 122.77, 122.28, 122.22, 119.36, 119.25, 116.22, 113.23, 112.93, 110.61, 109.71, 109.41, 109.20, 105.97, 84.48, 80.06, 75.70, 43.49, 43.13, 31.81, 29.68, 29.46, 29.44, 29.32, 29.22, 28.93, 28.90, 27.22, 22.62, 14.08. HRMS (EI) calcd for $C_{48}H_{58}N_6$+H: 719.4796 $[M+H]^+$; found: 719.4808.



3-Amino-6-(1-(9-(cyclohexylmethyl)-6-ethynyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (dimer-6MeCy) – Dimer-6MeCy was synthesized following the general procedure for the preparation of amino-alkynyl-crescent dimers using amino-carbazole **8a** (1.46 g, 5 mmol, 1 equiv.), azido-carbazole **7d-TMS** (2.20 g, 5.5 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (125 mg, 0.5 mmol, 0.1 equiv.), TBTA (265 mg, 0.5 mmol, 0.1 equiv.), and sodium ascorbate (396 mg, 1 mmol, 0.2 equiv.). Crude **dimer-6MeCy** was purified by column chromatography (SiO_2) using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (2.60 g, 4.2 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 1.6 Hz, 1H), 8.44 (d, J = 2.2 Hz, 1H), 8.32 (s, 1H), 8.29 (s, 1H), 7.99 (dd, J = 8.4, 1.7 Hz, 1H), 7.93 (dd, J = 8.7, 2.1 Hz, 1H), 7.66 (dd, J = 8.5, 1.6 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.41 (t, J = 8.7 Hz, 2H), 7.25 (d, J = 8.5 Hz, 1H), 6.95 (dd, J = 8.5, 2.2 Hz, 1H), 4.26 (t, J = 7.3 Hz, 2H), 4.17 (d, J = 7.3 Hz, 2H), 3.69 (broad s, 2H), 3.12 (s, 1H), 2.13 – 1.98 (m, 1H), 1.88 (p, J = 7.4 Hz, 2H), 1.82 – 1.59 (m, 6H), 1.52 – 1.26 (m, 5H), 1.26 – 1.06 (m, 5H), 0.97 – 0.83 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.49, 139.96, 134.93, 133.51, 130.62, 129.67, 129.17, 125.03, 124.87, 122.85, 122.31, 122.29, 119.38, 119.35, 116.31, 113.26, 112.99, 110.68, 109.73, 109.51, 109.3, 105.98, 84.57, 80.1, 75.76, 49.75, 43.44, 38.37, 31.62, 31.56, 28.96, 26.91, 26.34, 25.87, 22.55, 14.0. HRMS (EI) calcd for $C_{41}H_{42}N_6$+H: 619.3544 $[M+H]^+$; found: 619.3555.

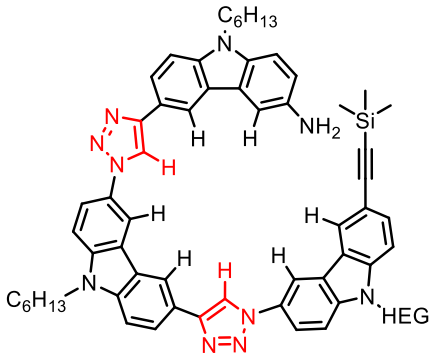


3-Amino-9-decyl-6-(1-(9-decyl-6-(1-(9-decyl-6-((trimethylsilyl)ethynyl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazole (NH_2-trimer-TMS-101010) – NH_2-trimer-TMS-101010 was synthesized following the general procedure for the preparationof amino-crescent trimers using **dimer-1010** (3.09 g, 4.3 mmol, 1 equiv.), azido-carbazole **7b-TMS** (2.10 g, 4.73 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (107 mg, 0.43 mmol, 0.1 equiv.), TBTA (228 mg, 0.43 mmol,0.1 equiv.), and sodium ascorbate (170 mg, 0.86 mmol, 0.2 equiv.). Crude **NH_2-trimer-TMS-101010** was purified by column chromatography on silica gel using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (3.84 g, 3.3 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 2.0 Hz, 1H), 8.56 (d, J = 1.6 Hz, 1H), 8.50 (d, J = 2.1 Hz, 1H), 8.43 (d, J = 2.1 Hz, 1H), 8.38 (s, 1H), 8.32 (s, 1H), 8.24 (s, 1H), 8.11 (dd, J = 8.5, 1.7 Hz, 1H), 7.97 (dd, J = 8.4, 1.7 Hz, 1H), 7.91 (dq, J = 7.4, 2.3 Hz, 2H), 7.60 (dd, J = 8.5, 1.6 Hz, 1H), 7.57 – 7.33 (m, 6H), 7.23 (d, J = 8.6 Hz, 1H), 6.91 (dd, J = 8.4, 2.3 Hz, 1H), 4.42 – 4.11 (m, 6H), 3.69 (s, 2H), 1.98 – 1.74 (m, 6H), 1.45 – 1.03 (m, 42H), 0.87 (t, J = 6.9 Hz, 9H), 0.29 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.99, 140.78, 140.56, 139.98, 139.39, 139.14, 138.39, 133.53, 131.73, 130.65, 130.18, 129.74, 129.17, 124.97, 124.81, 123.47, 122.98, 122.33, 121.91, 119.43, 119.26, 117.75, 116.32, 114.14, 113.41, 113.29, 110.68, 110.46, 110.02, 109,76, 109.50, 109.17, 108.86, 106.38, 106.12, 92.48, 92.06, 80.15, 43.57, 43.22, 43.20, 31.91, 29.76, 29.54, 29.53, 29.41, 29.30, 29.00, 28.98, 28.96, 27.31, 22.70, 14.16, 0.22. HRMS (EI) calcd for $C_{75}H_{94}N_{10}Si$+H: 1163.7505 $[M+H]^+$; found: 1163.7525.

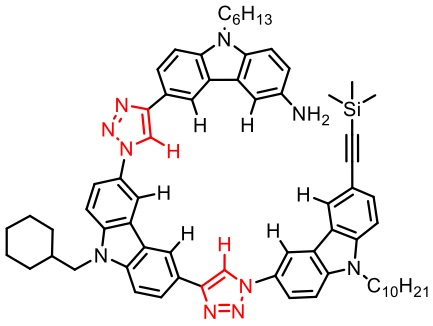


3-Amino-9-hexyl-6-(1-(9-hexyl-6-(1-(9-octadecyl-6-((trimethylsilyl)ethynyl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazole (NH_2-trimer-TMS-6618) – NH_2-trimer-TMS-6618 was synthesized following the general procedure for the formation of amino-crescent trimers by using **dimer-66** (1.26 g, 2.1 mmol, 1 equiv.), azido-carbazole **7c-TMS** (1.28 g, 2.3 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (52 mg, 0.21 mmol, 0.1 equiv.), TBTA (111 mg, 0.21 mmol, 0.1 equiv.), and sodium ascorbate (83 mg, 0.42 mmol, 0.2 equiv.). Crude **NH_2-trimer-TMS-6618** was purified by column chromatography on silica gel using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (1.86 g, 1.6 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.63 (s, 1H), 8.53 (s, 1H), 8.46 (s, 1H), 8.37 (s, 1H), 8.32 (s, 1H), 8.31 (s, 1H), 8.17 (d, J = 8.3 Hz, 1H), 8.06 – 7.90 (m, 3H), 7.65 (d, J = 8.1 Hz, 1H), 7.59 – 7.49 (m, 5H), 7.43 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 8.6 Hz, 1H), 7.25 (d, J = 8.7 Hz, peak partially overlaps with residual solvent), 6.95 (d, J = 7.7 Hz, 1H), 4.48 – 4.20 (m, 6H), 3.77 (s, 2H), 2.08 – 1.77 (m, 6H), 1.50 – 1.10 (m, 42H), 0.89 (t, J = 7.0 Hz, 9H), 0.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.99, 140.78, 140.56, 139.98, 139.39, 139.14, 138.39, 133.53, 131.73, 130.65, 130.18, 129.74, 129.17, 124.97, 124.81, 123.47, 122.98, 122.33, 121.91, 119.43, 119.26, 117.75, 116.32, 114.14, 113.41, 113.29, 110.68, 110.46, 110.02, 109.76, 109.50, 109.17, 108.86, 106.38, 106.12, 92.48, 92.06, 80.15, 43.54, 50.14, 43.79, 43.28, 31.99, 31.93, 31.60, 29.75, 29.72,

29.68, 29.62, 29.55, 29.47, 29.42, 29.32, 29.05, 28.98, 28.88, 27.28, 27.24, 27.00, 22.74, 22.69, 22.57, 14.18, 14.12, 14.02, 0.22. HRMS (EI) calcd for $C_{75}H_{94}N_{10}Si$+H: 1163.7505 $[M+H]^+$; found: 1163.7509.

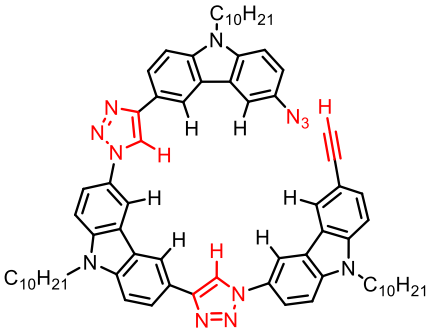


3-Amino-9-hexyl-6-(1-(9-hexyl-6-(1-(9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-6-((trimethylsilyl)ethynyl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazole (NH_2-trimer-TMS-66HEG) – NH_2-trimer-TMS-66HEG was synthesized following the general procedure for the formation of amino-crescent trimers using **dimer-66** (1.26 g, 2.1 mmol, 1 equiv.), azido-carbazole **7e-TMS** (1.39 g, 2.3 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (52 mg, 0.21 mmol, 0.1 equiv.), TBTA (111 mg, 0.21 mmol, 0.1 equiv.), and sodium ascorbate (83 mg, 0.42 mmol, 0.2 equiv.). Crude **NH_2-trimer-TMS-66HEG** was purified by column chromatography on silica gel using an eluent gradient of ethyl acetate to 5:1 ethyl acetate:acetone yielding pure product as a brown solid (1.82 g, 1.5 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 1.0 Hz, 1H), 8.60 (d, J = 1.3 Hz, 1H), 8.47 (d, J = 1.3 Hz, 1H), 8.43 (d, J = 1.4 Hz, 1H), 8.38 (s, 1H), 8.29 (s, 1H), 8.26 (d, J = 1.0 Hz, 1H), 8.15 (d, J = 5.9 Hz, 1H), 7.98 (dd, J = 5.6, 1.1 Hz, 1H), 7.96 – 7.88 (m, 3H), 7.62 (dd, J = 5.7, 1.1 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.41 – 7.36 (m, 2H), 7.22 (d, J = 5.6 Hz, 1H), 6.94 (dd, J = 5.6, 1.5 Hz, 1H), 4.49 (t, J = 3.8 Hz, 2H), 4.33 (t, J = 4.8 Hz, 2H), 4.23 (t, J = 4.9 Hz, 2H), 3.89 (t, J = 3.8 Hz, 2H), 3.71 – 3.43 (m, 20H), 3.35 (s, 3H), 1.89 (m, 4H), 1.51 – 1.22 (m, 12H), 0.98 – 0.81 (m, 6H), 0.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.99, 140.78, 140.56, 139.98, 139.39, 139.14, 138.39, 133.53, 131.73, 130.65, 130.18, 129.74, 129.17, 124.97, 124.81, 123.47, 122.98, 122.33, 121.91, 119.43, 119.26, 117.75, 116.32, 114.14, 113.41, 113.29, 110.68, 110.46, 110.02, 109.76, 109.5, 109.17, 108.86, 106.38, 106.12, 92.48, 92.06, 80.15, 72.08, 71.04, 70.75, 70.70, 70.62, 70.61, 70.61, 70.60, 69.45, 59.09, 44.10, 43.55, 43.32, 31.95, 31.61, 29.09, 29.08, 27.34, 27.09, 22.79, 22.57, 14.16, 14.06, 0.22. HRMS (EI) calcd for $C_{70}H_{84}N_{10}O_6Si$+Na: 1211.6237 $[M+Na]^+$; found: 1211.6267.

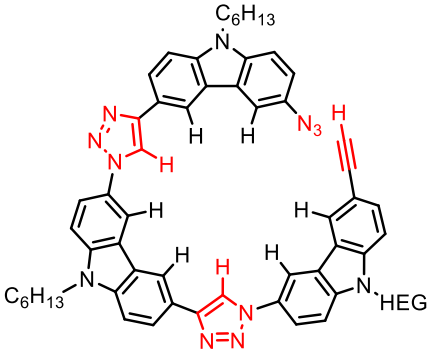


3-Amino-6-(1-(9-(cyclohexylmethyl)-6-(1-(9-decyl-6-((trimethylsilyl)ethynyl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (NH_2-trimer-TMS-6MeCy10) – NH_2-trimer-TMS-6MeCy10 was prepared following the general procedure for the formation of amino-crescent trimers using **dimer-6MeCy** (2.60 g, 4.2 mmol, 1 equiv.), azido-carbazole **7b-TMS** (2.04 g, 4.6 mmol, 1.1 equiv.), $CuSO_4$•5 H_2O (105 mg, 0.42 mmol, 0.1 equiv.), TBTA (223 mg, 0.42 mmol, 0.1 equiv.), and sodium ascorbate (166 mg, 0.84 mmol, 0.2 equiv.). Crude **NH_2-trimer-TMS-6MeCy10** was purified by column chromatography on silica gel using an eluent gradient of dichloromethane to 97:3 dichloromethane:acetone yielding pure product as a brown solid (3.30 g, 3.1 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, J = 3.2 Hz, 1H), 8.62 (d, J = 3.9 Hz, 1H), 8.51 (d, J = 5.0 Hz, 1H), 8.46 (s, 1H), 8.37 (d, J = 4.2 Hz, 1H), 8.31 (d, J = 4.8 Hz, 2H), 8.16 (d, J = 4.7 Hz, 1H), 8.00 (d,

J = 5.4 Hz, 1H), 7.95 (s, 1H), 7.66 (t, *J* = 6.0 Hz, 2H), 7.57 – 7.50 (m, 4H), 7.47 – 7.35 (m, 3H), 7.24 (d, *J* = 5.4 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 4.33 (t, *J* = 4.8 Hz, 2H), 4.26 (t, *J* = 4.3 Hz, 2H), 4.21 (s, 2H), 2.08 (s, 1H), 1.95 – 1.82 (m, 2H), 1.82 – 1.68 (m, 2H), 1.48 – 1.09 (m, 30H), 0.89 (t, *J* = 4.6 Hz, 6H), 0.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.99, 140.78, 140.57, 139.99, 139.39, 139.15, 138.39, 133.54, 131.73, 130.65, 130.18, 129.74, 129.18, 124.97, 124.82, 123.48, 122.98, 122.34, 121.91, 119.43, 119.26, 117.75, 116.33, 114.15, 113.41, 113.30, 110.69, 110.47, 110.02, 109.77, 109.50, 109.18, 108.86, 106.39, 106.12, 92.49, 92.07, 80.15, 49.76, 43.44, 43.16, 38.38, 31.81, 31.62, 31.57, 29.47, 29.35, 29.22, 28.96, 28.90, 27.23, 26.92, 26.34, 25.87, 22.64, 22.55, 14.09, 14.01, 0.22. HRMS (EI) calcd for $C_{68}H_{78}N_{10}Si$+H: 1063.6253 $[M+H]^+$; found: 1063.6275.

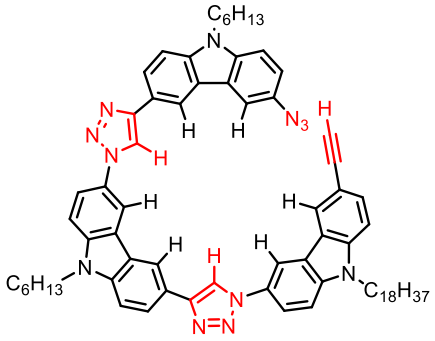


3-Azido-9-decyl-6-(1-(9-decyl-6-(1-(9-decyl-6-ethynyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazole (trimer-101010) – Trimer-101010 was synthesized following the general procedure for the formation of azido-crescent trimers using **NH_2-trimer-TMS-101010** (1.16 g, 1 mmol, 1 equiv.), *p*-toluenesulfonic acid (570 mg, 3 mmol, 3 equiv.), sodium nitrite (76 mg, 1.1 mmol, 1.1 equiv.), and sodium azide (78 mg, 1.2 mmol, 1.2 equiv.). Crude **trimer-101010** was purified by column chromatography on silica gel using 97:3 dichloromethane:acetone as eluent yielding pure product as a brown solid (1.07 g, 0.96 mmol, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.58 (s, 1H), 8.43 (s, 1H), 8.37 (s, 1H), 8.33 (s, 1H), 8.31 (s, 1H), 8.23 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 2H), 7.76 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 4H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.35 (dd, *J* = 8.7, 3.4 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.48 – 4.01 (m, 6H), 3.15 (s, 1H), 2.06 – 1.74 (m, 6H), 1.52 – 1.05 (m, 42H), 0.86 (t, *J* = 6.7 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.68, 141.02, 140.84, 140.48, 139.94, 139.89, 134.90, 133.43, 130.59, 129.66, 129.30, 129.07, 125.00, 124.82, 124.01, 122.78, 122.58, 122.44, 122.29, 122.23, 121.93, 119.37, 119.26, 116.22, 113.23, 112.93, 110.64, 110.62, 109.72, 109.42, 109.41, 109.25, 109.21, 105.98, 84.49, 80.06, 75.71, 43.49, 43.14, 31.82, 29.69, 29.46, 29.44, 29.33, 29.22, 28.94, 28.90, 27.22, 22.63, 14.09. HRMS (EI) calcd for $C_{72}H_{84}N_{12}$: 1116.7432 $[M]^+$; found: 1116.7443.

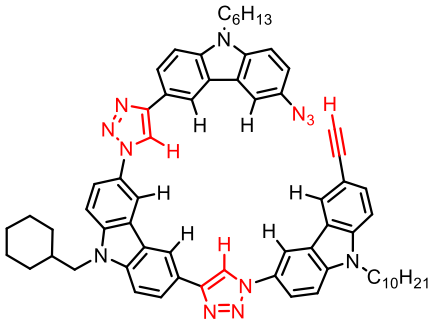


3-Azido-6-(1-(6-(1-(6-ethynyl-9-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (trimer-66HEG) – Trimer-66HEG was synthesized following the general procedure for the formation of azido-crescent trimers using **NH_2-trimer-TMS-66HEG** (1.21 g, 1 mmol, 1 equiv.), *p*-toluenesulfonic acid (570 mg, 3 mmol, 3 equiv.), sodium nitrite (76 mg, 1.1 mmol, 1.1 equiv.), and sodium azide (78 mg, 1.2 mmol, 1.2 equiv.). Crude **trimer-66HEG** was purified by column chromatography on silica gel using 5:1 ethyl acetate:acetone as eluent yielding pure product as a brown solid (1.16 g,

0.9 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.63 (s, 1H), 8.55 (s, 1H), 8.47 (s, 1H), 8.40 (s, 1H), 8.34 (s, 1H), 8.30 (s, 1H), 8.23 – 8.11 (m, 2H), 8.06 – 7.89 (m, 3H), 7.64 (t, J = 5.4 Hz, 2H), 7.59 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.39 (d, J = 1.9 Hz, 1H), 7.25 (d, J = 5.7 Hz, 1H), 4.55 (t, J = 3.6 Hz, 2H), 4.40 (t, J = 5.1 Hz, 2H), 4.27 (t, J = 4.8 Hz, 2H), 3.92 (t, J = 3.4 Hz, 2H), 3.77 – 3.43 (m, 20H), 3.36 (s, 3H), 3.12 (s, 1H), 2.08 – 1.79 (m, 4H), 1.44 – 1.20 (m, 12H), 0.90 (dt, J = 7.9, 4.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.99, 140.79, 140.57, 139.99, 139.39, 139.15, 138.39, 133.53, 131.73, 130.66, 130.18, 129.75, 129.18, 124.97, 124.81, 123.48, 122.99, 122.34, 121.92, 119.44, 119.27, 119.07, 117.76, 116.32, 114.15, 113.41, 113.30, 110.68, 110.47, 110.03, 109.77, 109.51, 109.18, 108.87, 106.38, 106.12, 85.11, 74.61, 72.08, 71.04, 70.76, 70.70, 70.63, 70.62, 70.61, 70.61, 69.46, 59.10, 44.10, 43.56, 43.33, 31.95, 31.61, 29.09, 29.09, 27.35, 27.09, 22.80, 22.57, 14.17, 14.06. HRMS (EI) calcd for $C_{67}H_{74}N_{12}O_6$: 1165.5746 $[M]^+$; found: 1165.5767.



3-Azido-6-(1-(6-(1-(6-ethynyl-9-octadecyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (trimer-6618) – Trimer-6618 was synthesized following the general procedure for the formation of azido-crescent trimers using **NH_2-trimer-TMS-6618** (1 mmol, 1 equiv.), *p*-toluenesulfonic acid (570 mg, 3 mmol, 3 equiv.), sodium nitrite (76 mg, 1.1 mmol, 1.1 equiv.), and sodium azide (78 mg, 1.2 mmol, 1.2 equiv.). Crude **trimer-6618** was purified by column chromatography on silica gel using 97:3 dichloromethane:acetone as eluent yielding pure product as a brown solid (1.20 g, 0.95 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.64 (s, 1H), 8.57 (s, 1H), 8.48 (s, 1H), 8.42 – 8.29 (m, 2H), 8.18 (d, J = 7.8 Hz, 1H), 8.06 – 7.93 (m, 3H), 7.66 (d, J = 8.3 Hz, 1H), 7.62 – 7.49 (m, 5H), 7.45 (d, J = 8.9 Hz, 1H), 7.39 (d, J = 8.7 Hz, 1H), 7.25 (s, 1H), 6.96 (dd, J = 8.3, 2.1 Hz, 1H), 4.41 (t, J = 5.2 Hz, 2H), 4.36 (t, J = 7.5 Hz, 2H), 4.28 (t, J = 7.2 Hz, 2H), 3.12 (s, 1H), 2.08 – 1.82 (m, 6H), 1.48 – 1.15 (m, 42H), 1.00 – 0.80 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.00, 140.79, 140.56, 139.98, 139.39, 139.15, 138.40, 133.53, 131.74, 130.68, 130.65, 130.19, 129.74, 129.18, 124.98, 124.81, 123.47, 122.99, 122.34, 121.91, 119.44, 119.27, 117.75, 116.32, 114.15, 113.42, 113.30, 110.69, 110.46, 110.03, 109.76, 109.50, 109.17, 108.86, 106.39, 106.12, 85.12, 74.82, 50.14, 43.79, 43.55, 43.28, 31.99, 31.94, 31.60, 29.76, 29.73, 29.68, 29.63, 29.55, 29.47, 29.43, 29.32, 29.06, 28.99, 28.88, 27.28, 27.24, 27.00, 22.75, 22.70, 22.57, 14.18, 14.13, 14.03. HRMS (EI) calcd for $C_{72}H_{84}N_{12}$: 1116.6942 $[M]^+$; found: 1116.6952.



3-Azido-6-(1-(9-(cyclohexylmethyl)-6-(1-(9-decyl-6-ethynyl-carbazol-3-yl)-1,2,3-triazol-4-yl)-carbazol-3-yl)-1,2,3-triazol-4-yl)-9-hexyl-carbazole (trimer-6MeCy10) – Trimer-6MeCy10 was synthesized following the general procedure for the formation of azido-crescent trimers using **NH_2-trimer-TMS-6MeCy10** (1 mmol, 1 equiv.), *p*-toluenesulfonic acid (570 mg, 3 mmol, 3 equiv.), sodium nitrite (76 mg, 1.1 mmol, 1.1 equiv.), and sodium azide (78 mg, 1.2 mmol, 1.2 equiv.). Crude **trimer-6MeCy10** was

purified by column chromatography on silica gel using 97:3 dichloromethane:acetone as eluent yielding pure product as a brown solid (1.10 g, 0.95 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 1.9 Hz, 1H), 8.67 (s, 1H), 8.52 (s, 1H), 8.45 (s, 1H), 8.35 (d, J = 3.2 Hz, 2H), 8.31 (dd, J = 4.6, 1.5 Hz, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.95 (t, J = 8.1 Hz, 2H), 7.84 (s, 1H), 7.66 (t, J = 8.4 Hz, 2H), 7.59 – 7.46 (m, 3H), 7.43 – 7.36 (m, 2H), 7.16 (d, J = 8.6 Hz, 1H), 4.32 (q, J = 7.9, 7.4 Hz, 4H), 4.20 (d, J = 7.4 Hz, 2H), 3.12 (s, 1H), 2.19 – 1.97 (m, 1H), 1.97 – 1.84 (m, 2H), 1.84 – 1.64 (m, 2H), 1.50 – 1.08 (m, 30H), 0.89 (dt, J = 7.8, 4.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.00, 140.79, 140.57, 139.99, 139.40, 139.16, 138.40, 133.54, 131.73, 130.66, 130.19, 129.75, 129.19, 124.98, 124.82, 123.49, 122.99, 122.35, 121.91, 119.51, 119.43, 119.27, 117.76, 116.33, 114.16, 113.42, 113.30, 110.69, 110.47, 110.03, 109.78, 109.51, 109.19, 108.86, 106.39, 106.12, 85.56, 74.61, 49.77, 43.45, 43.17, 38.39, 31.81, 31.63, 31.58, 29.48, 29.36, 29.23, 28.97, 28.90, 27.23, 26.93, 26.35, 25.87, 22.64, 22.56, 14.09, 14.02. HRMS (EI) calcd for $C_{65}H_{68}N_{12}$: 1016.569 $[M]^{+}$; found: 1016.5709.

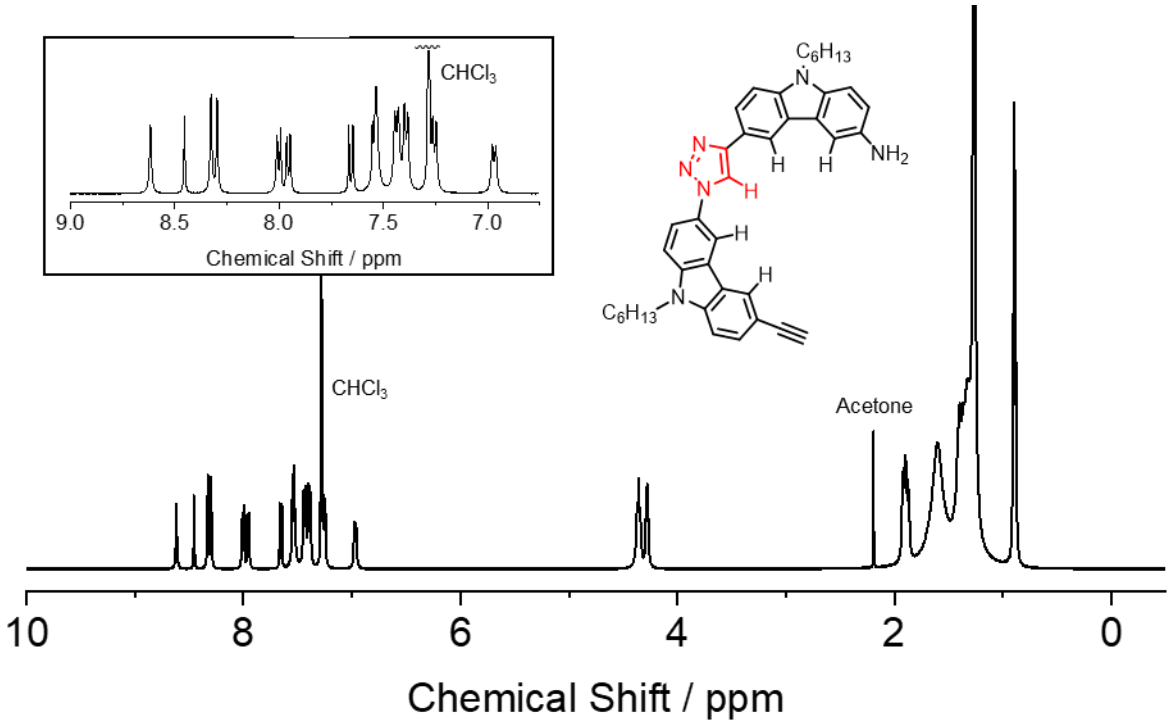


Figure S45. ^{1}H NMR spectrum of **dimer-66**.

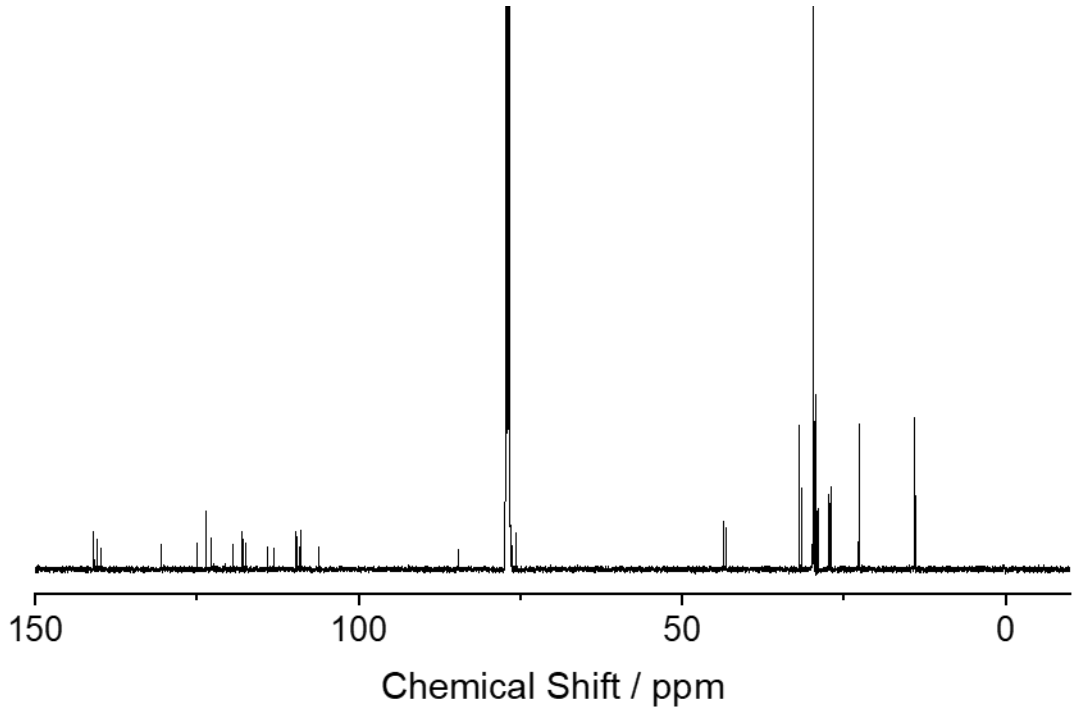


Figure S46. ^{13}C NMR spectrum of **dimer-66**.

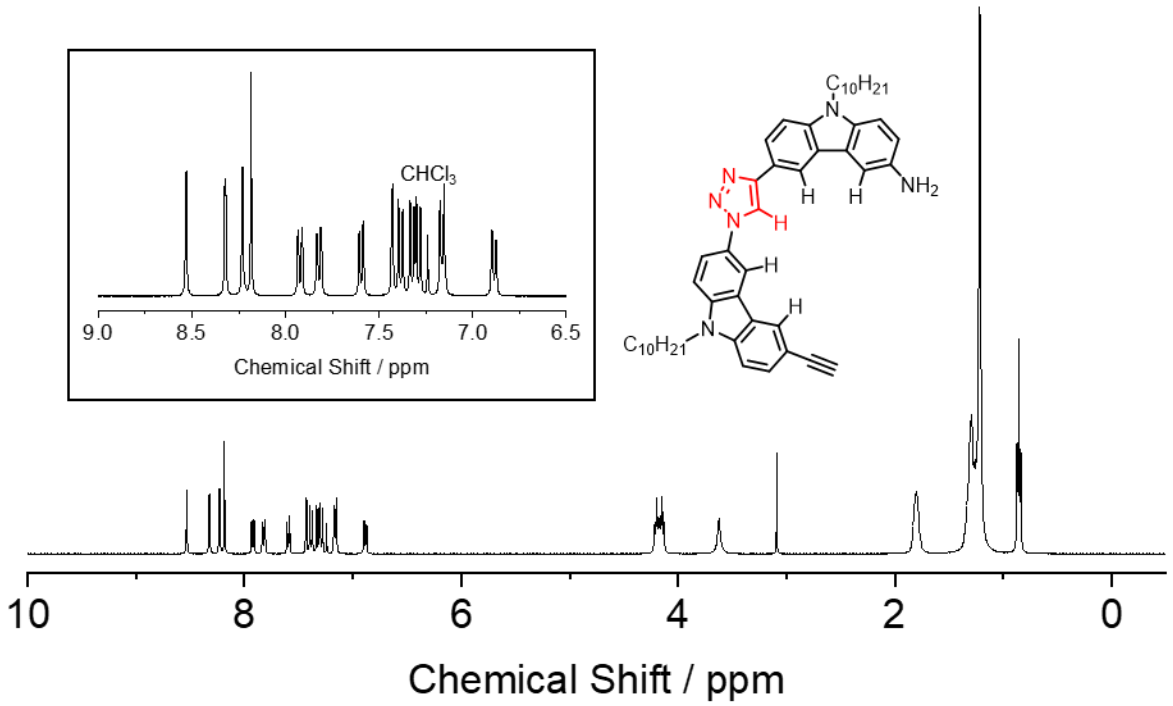


Figure S47. ^{1}H NMR spectrum of **dimer-1010**.

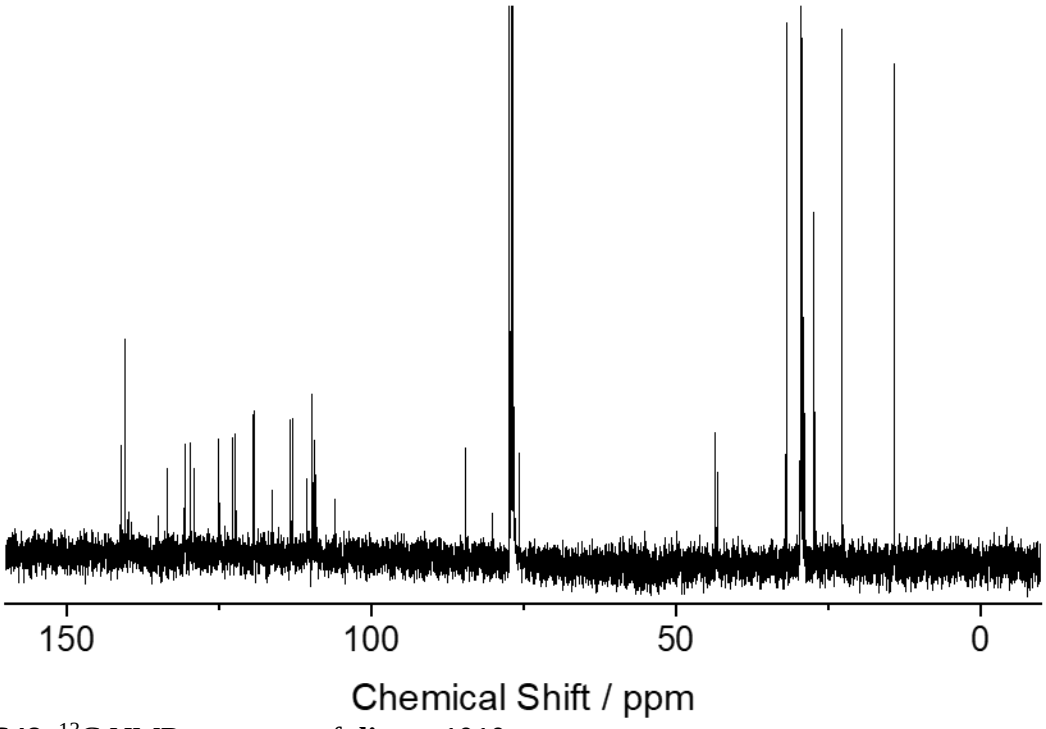


Figure S48. ^{13}C NMR spectrum of **dimer-1010**.

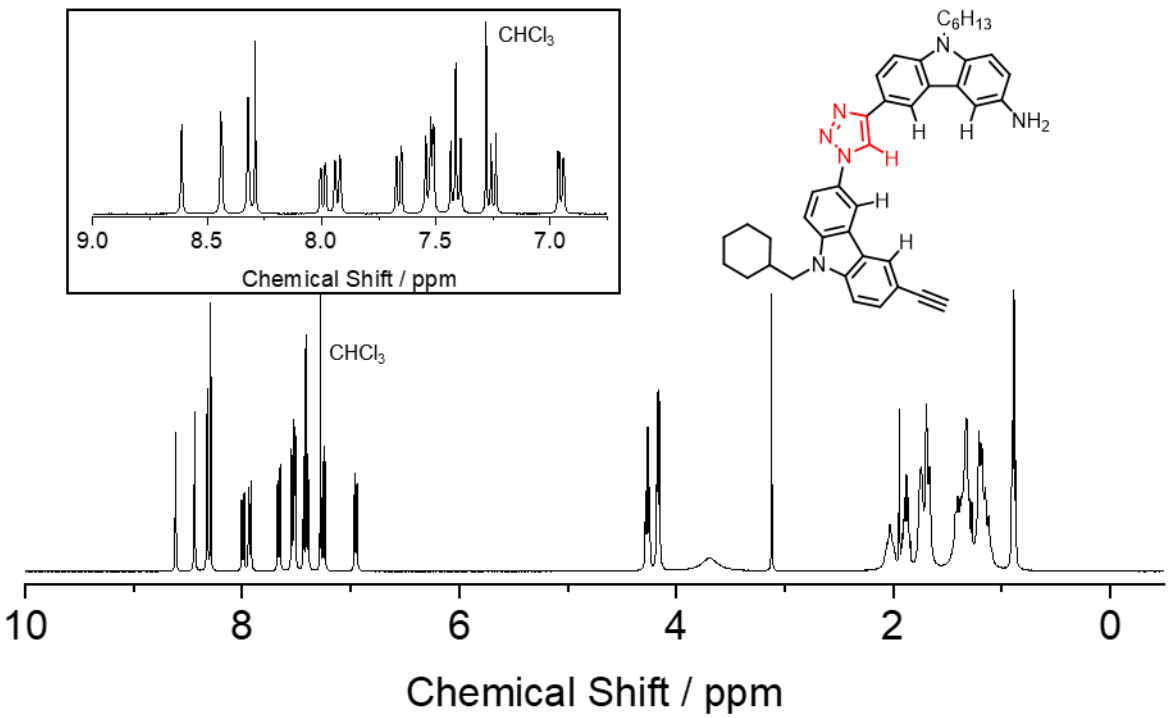


Figure S49. ^{1}H NMR spectrum of **dimer-6MeCy**.

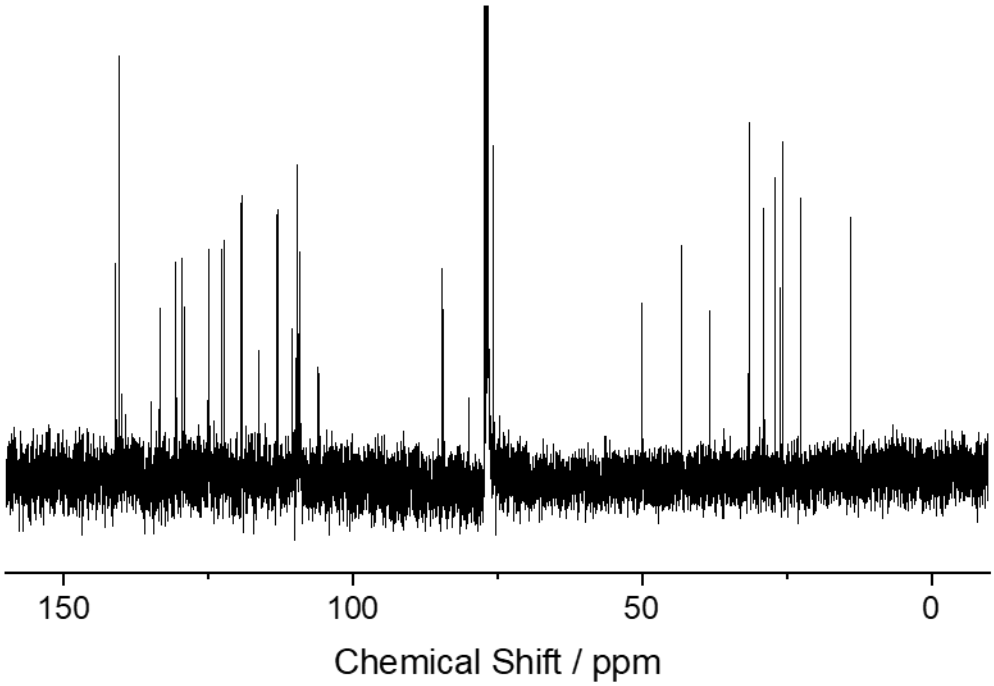


Figure S50. ^{13}C NMR spectrum of **dimer-6MeCy**.

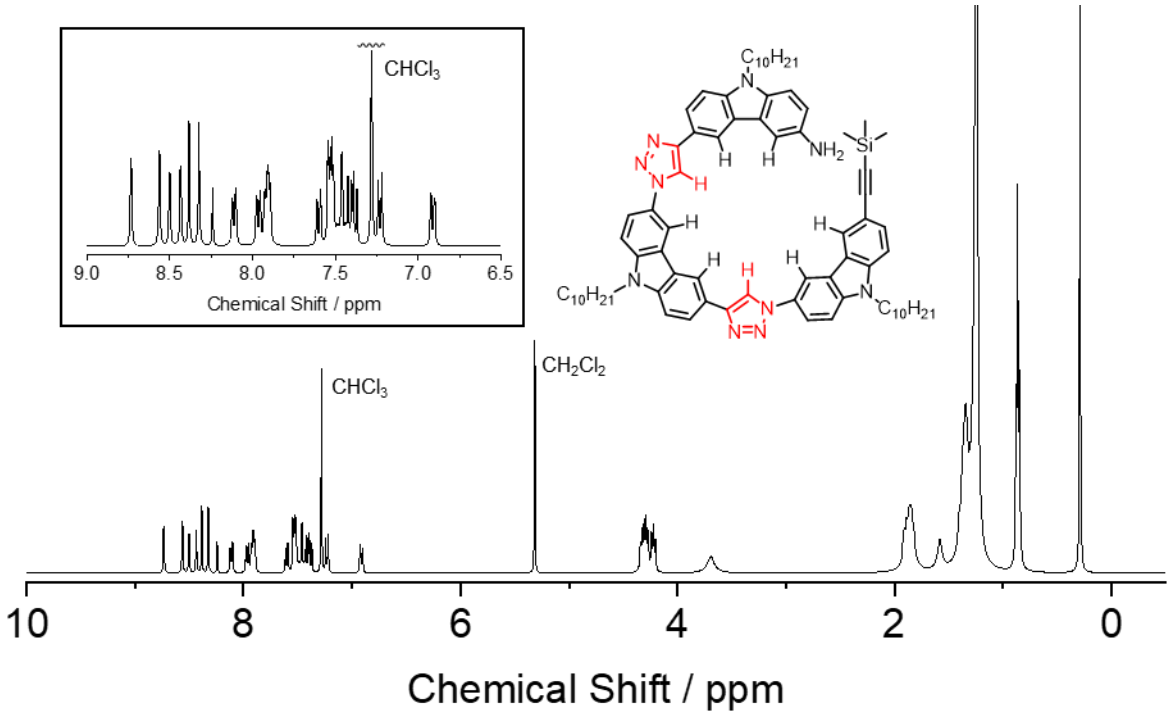


Figure S51. ^{1}H NMR spectrum of **NH_2-trimer-TMS-101010**.

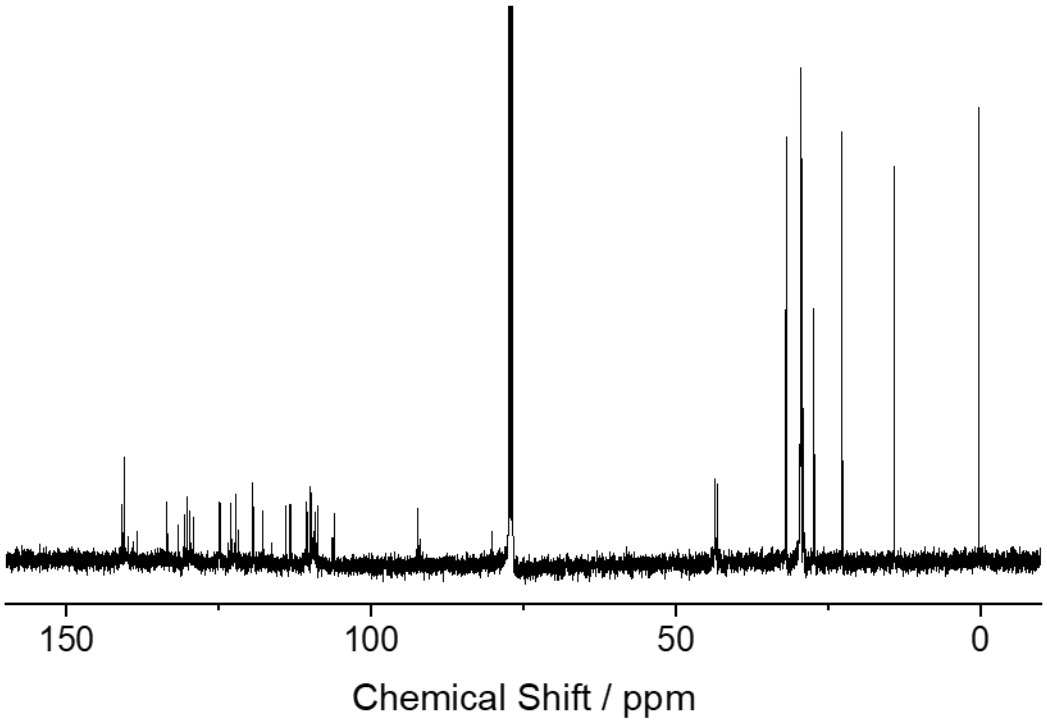


Figure S52. ^{13}C NMR spectrum of **NH_2-trimer-TMS-101010**.

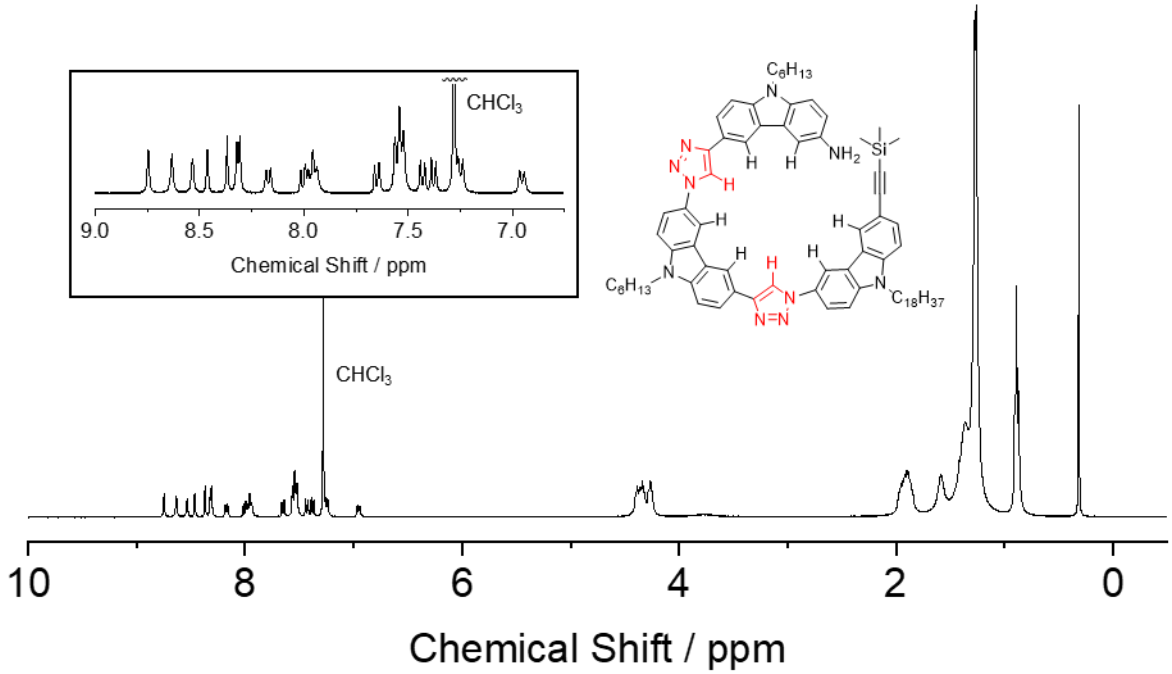


Figure S53. ^{1}H NMR spectrum of **NH_2-trimer-TMS-6618**.

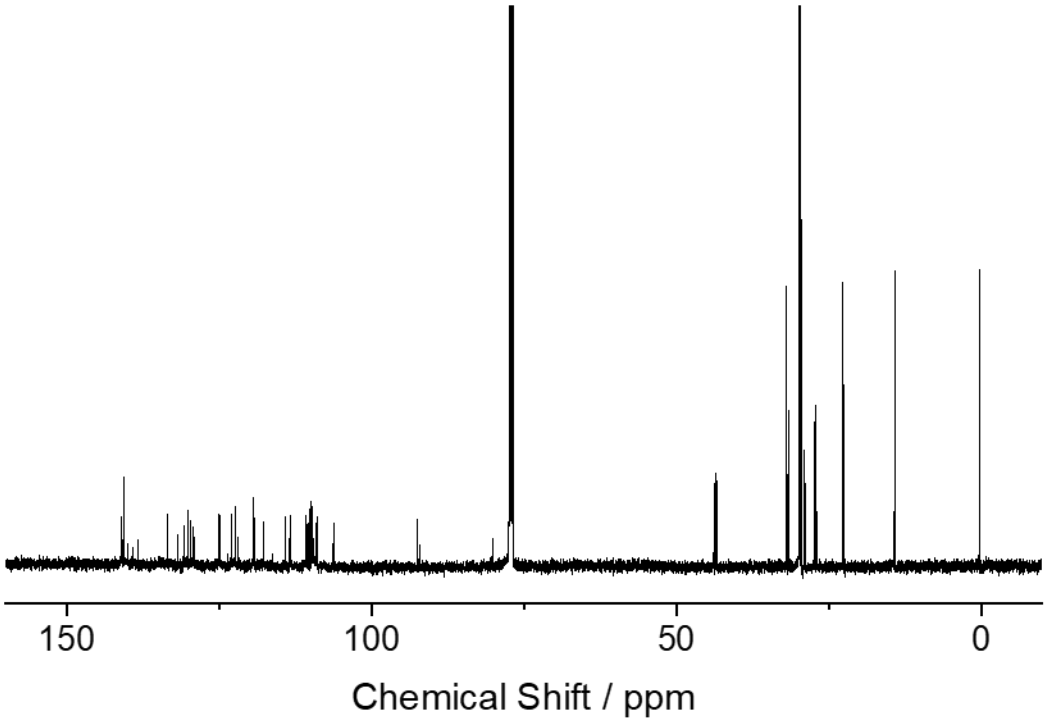


Figure S54. ^{13}C NMR spectrum of **NH_2-trimer-TMS-6618**.

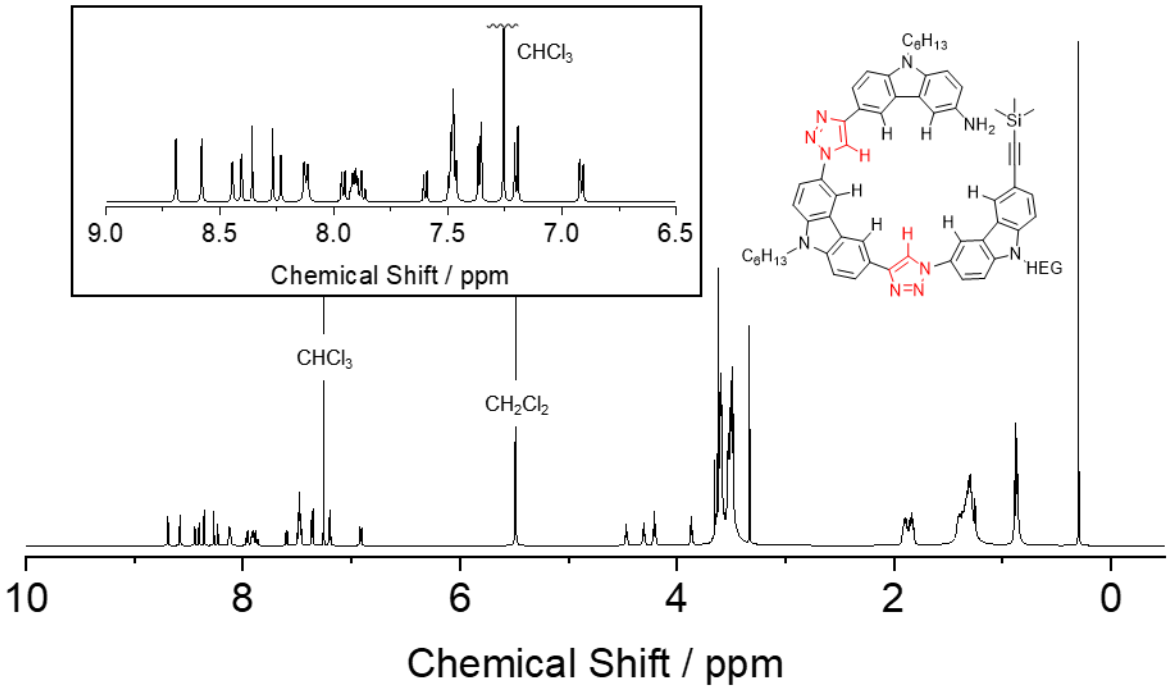


Figure S55. ^{1}H NMR spectrum of **NH_2-trimer-TMS-66HEG**.

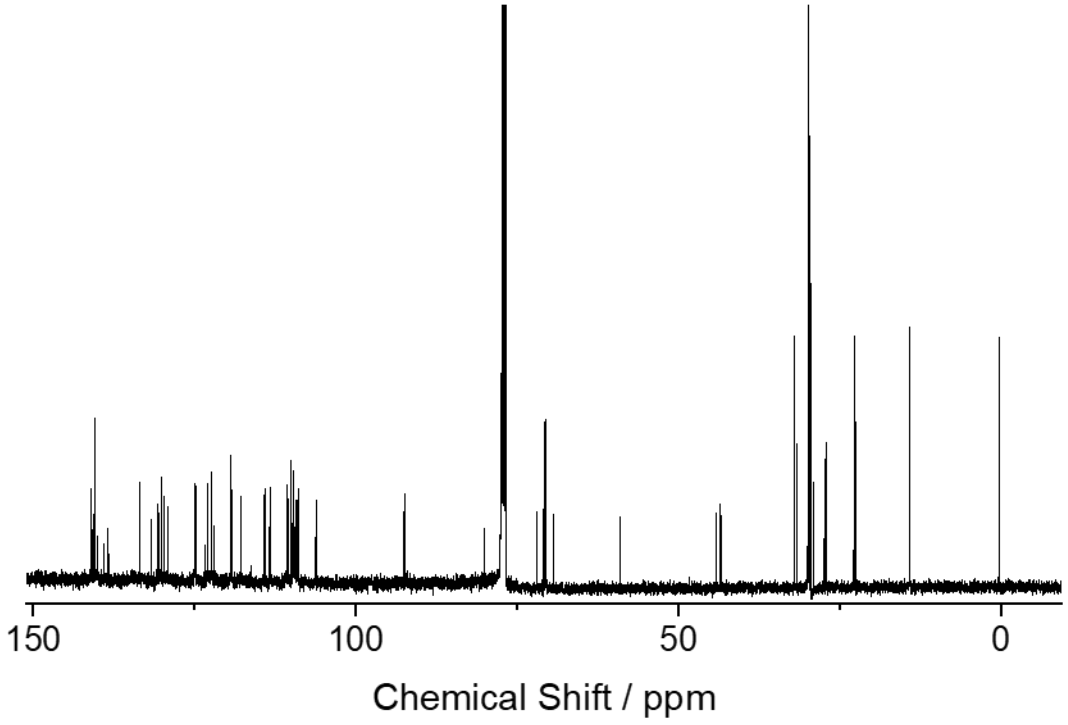


Figure S56. ^{13}C NMR spectrum of **NH_2-trimer-TMS-66HEG**.

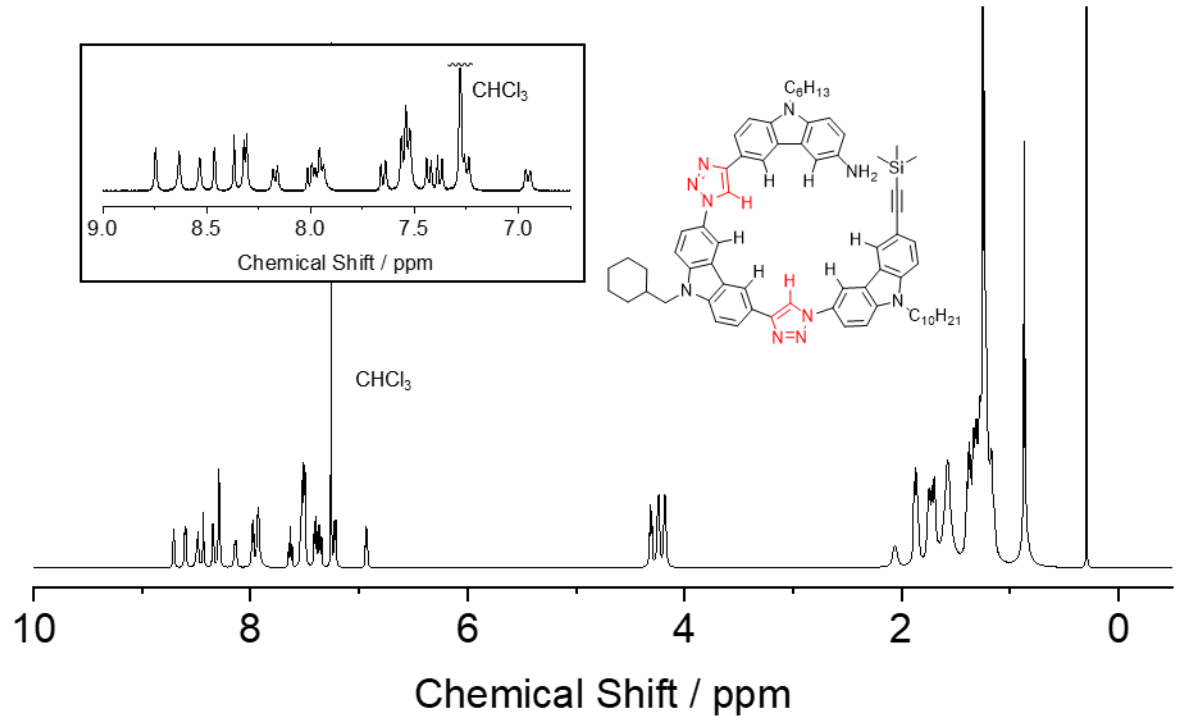


Figure S57. ^{1}H NMR spectrum of **NH_2-trimer-TMS-6MeCy10**.

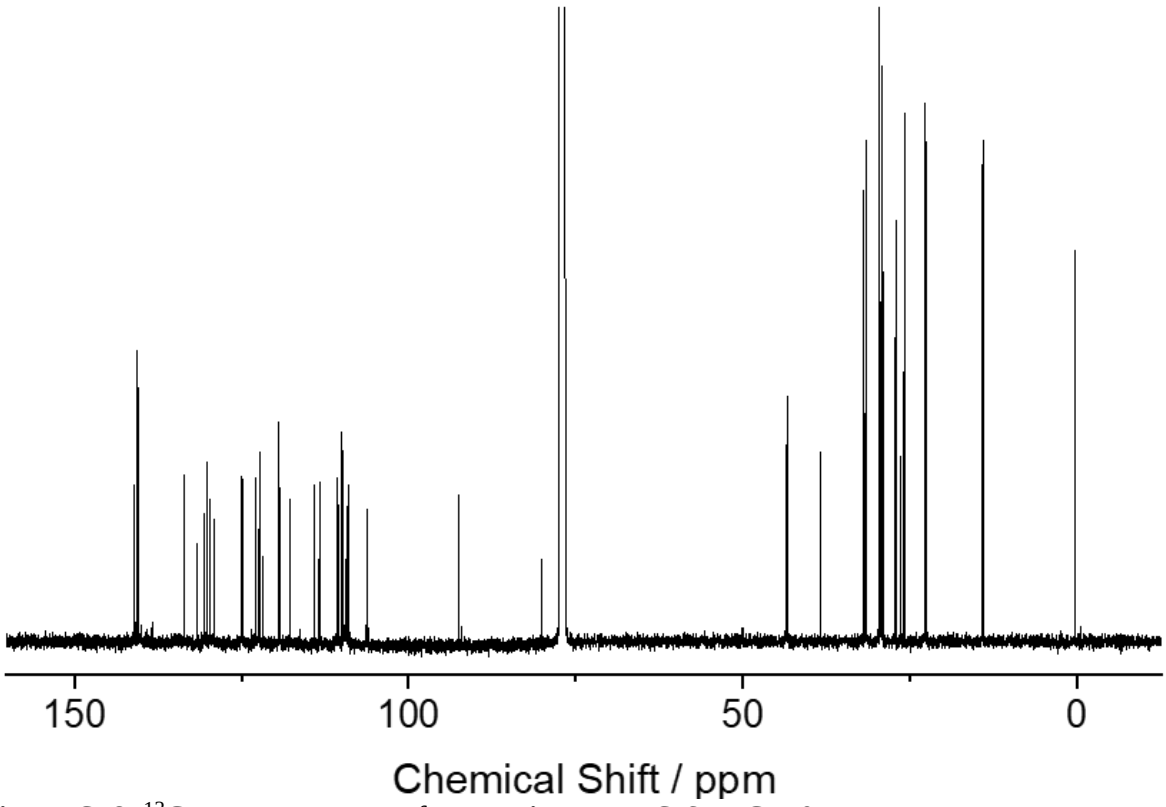


Figure S58. ^{13}C NMR spectrum of **NH_2-trimer-TMS-6MeCy10**.

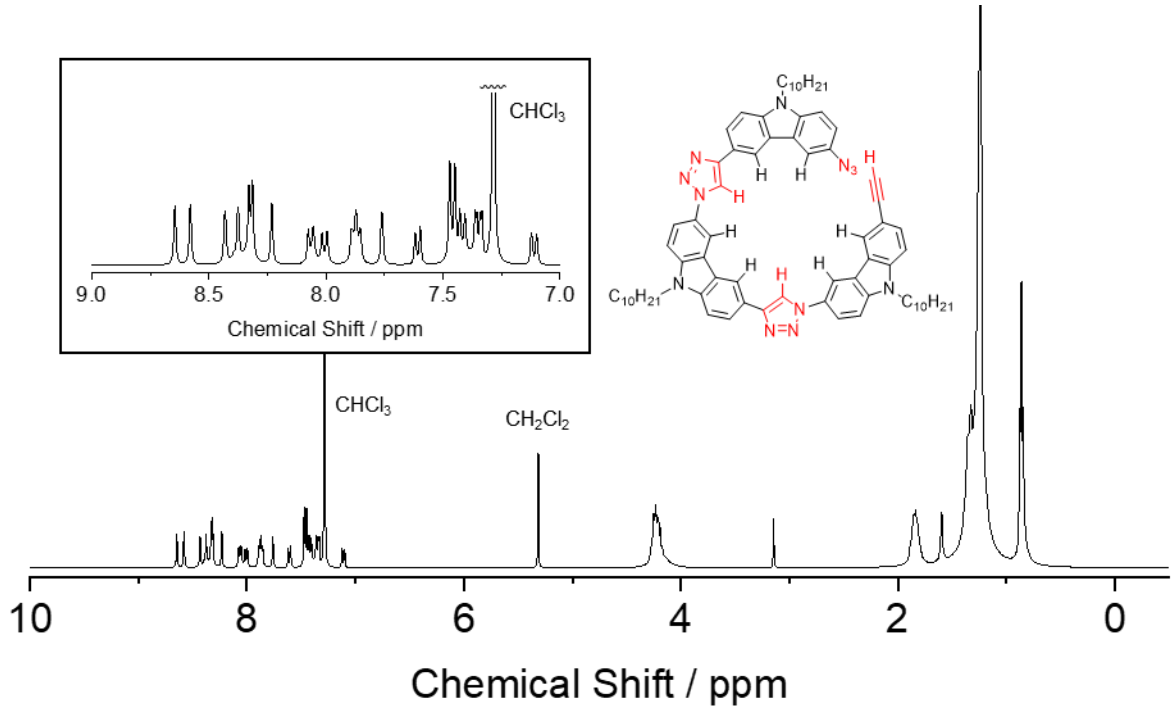


Figure S59. ^{1}H NMR spectrum of **trimer-101010**.

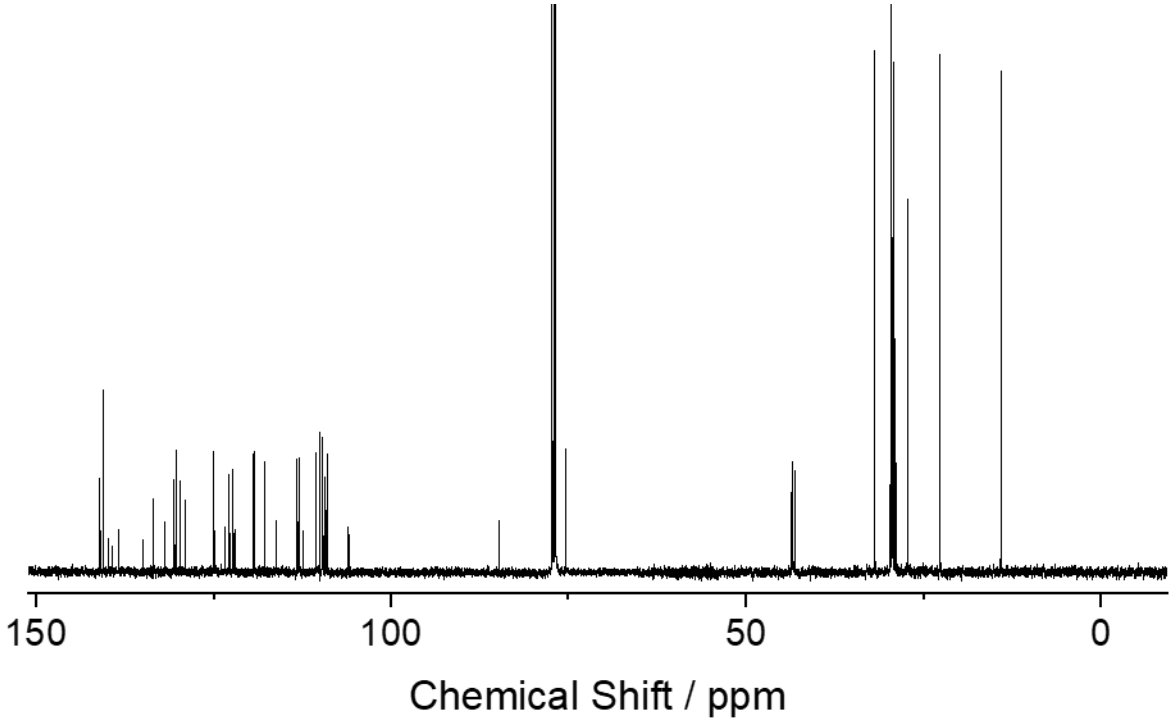


Figure S60. ^{13}C NMR spectrum of **trimer-101010**.

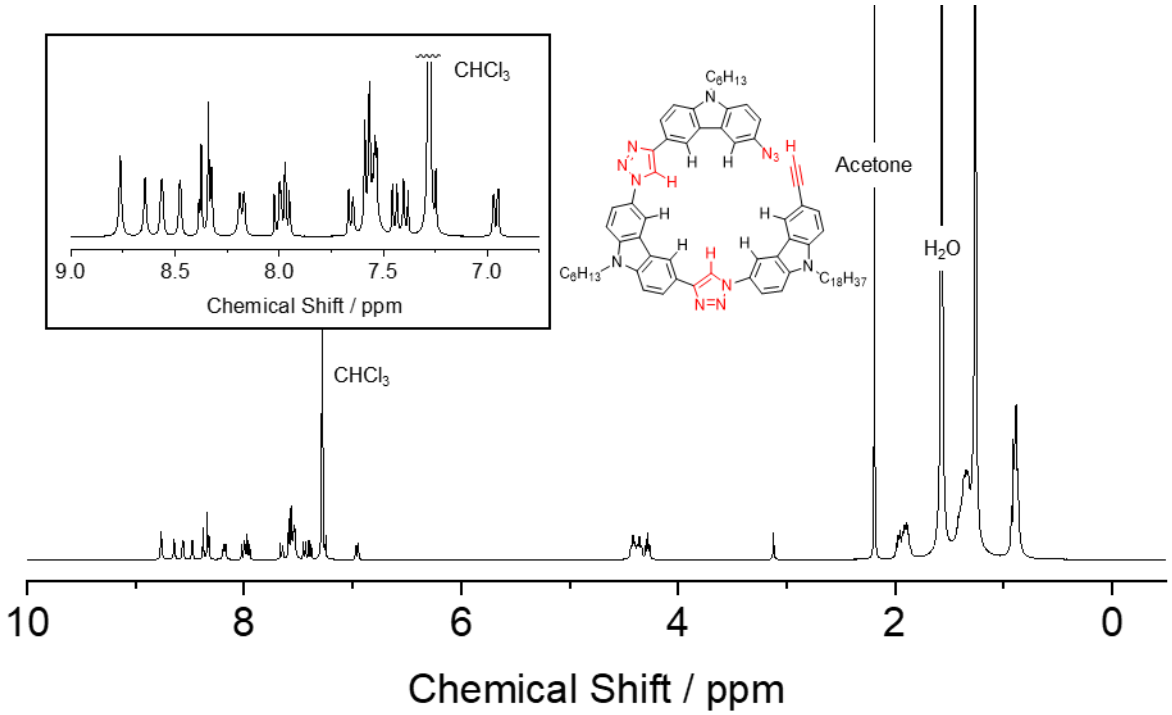


Figure S61. ^{1}H NMR spectrum of **trimer-6618**.

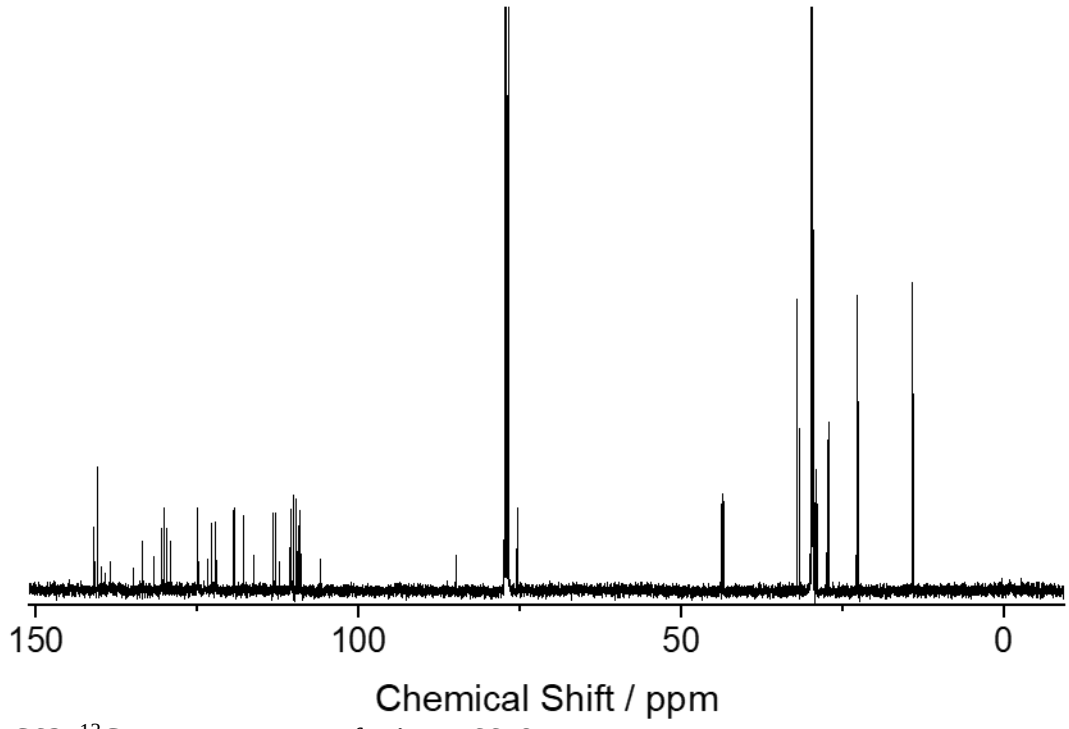


Figure S62. ^{13}C NMR spectrum of **trimer-6618**.

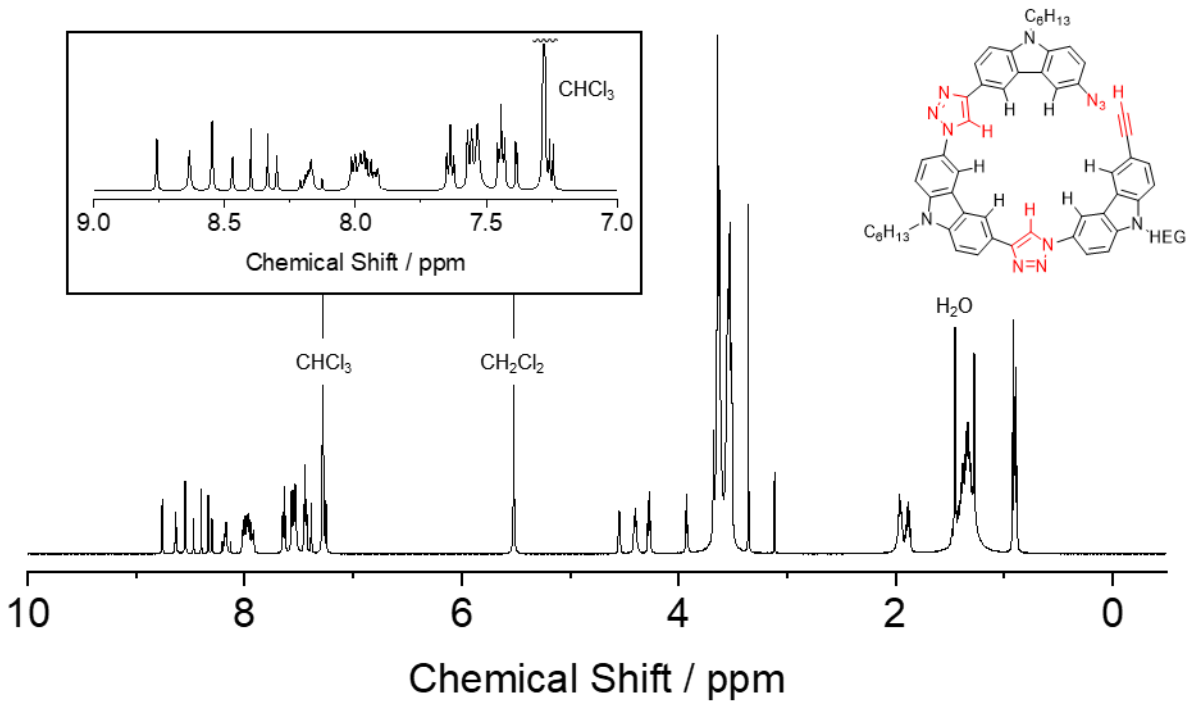


Figure S63. ^{1}H NMR spectrum of **trimer-66HEG**.

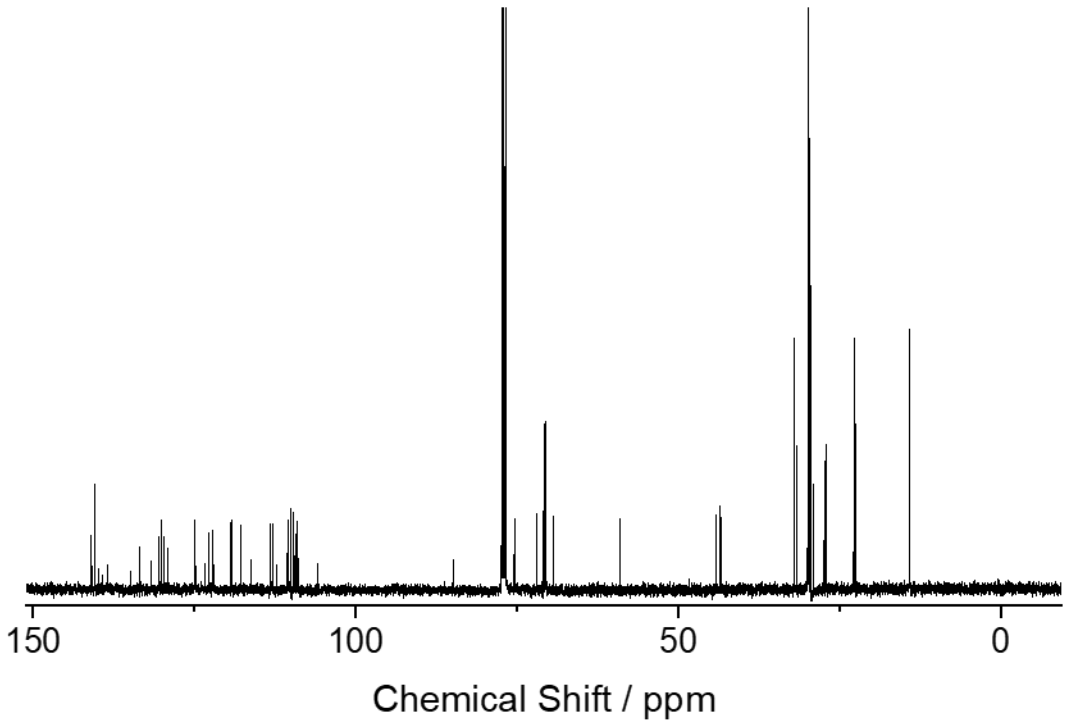


Figure S64. ^{13}C NMR spectrum of **trimer-66HEG**.

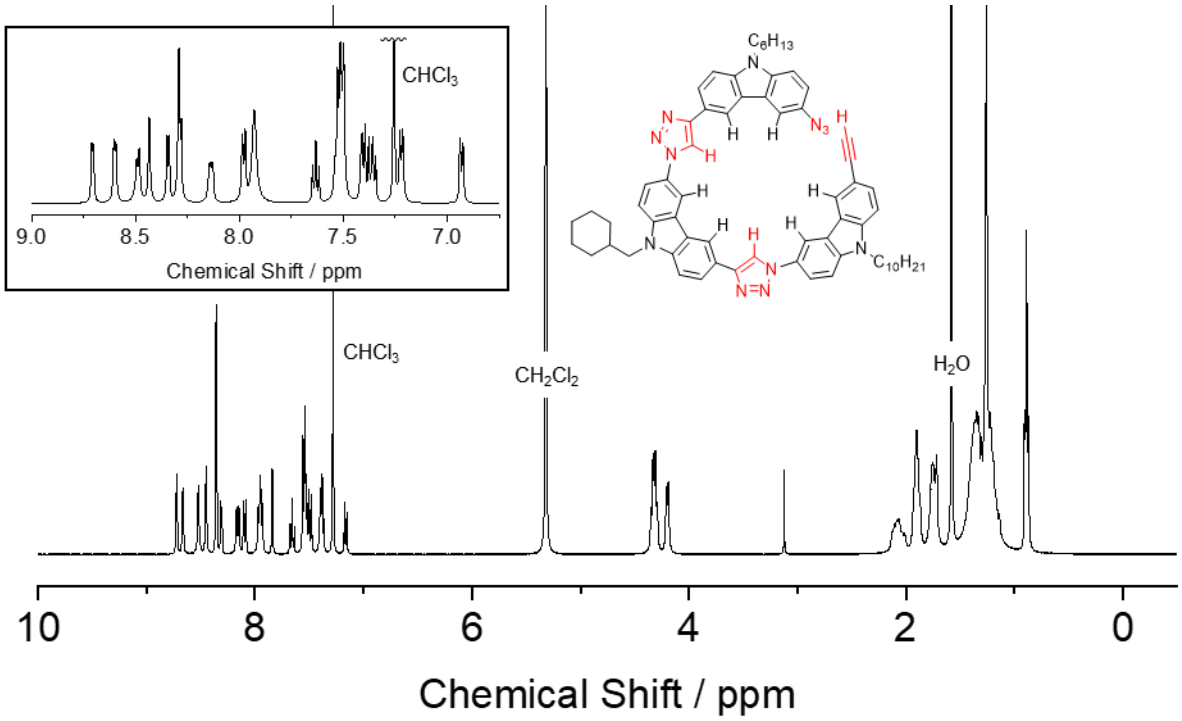


Figure S65. ^{1}H NMR spectrum of **trimer-6MeCy10**.

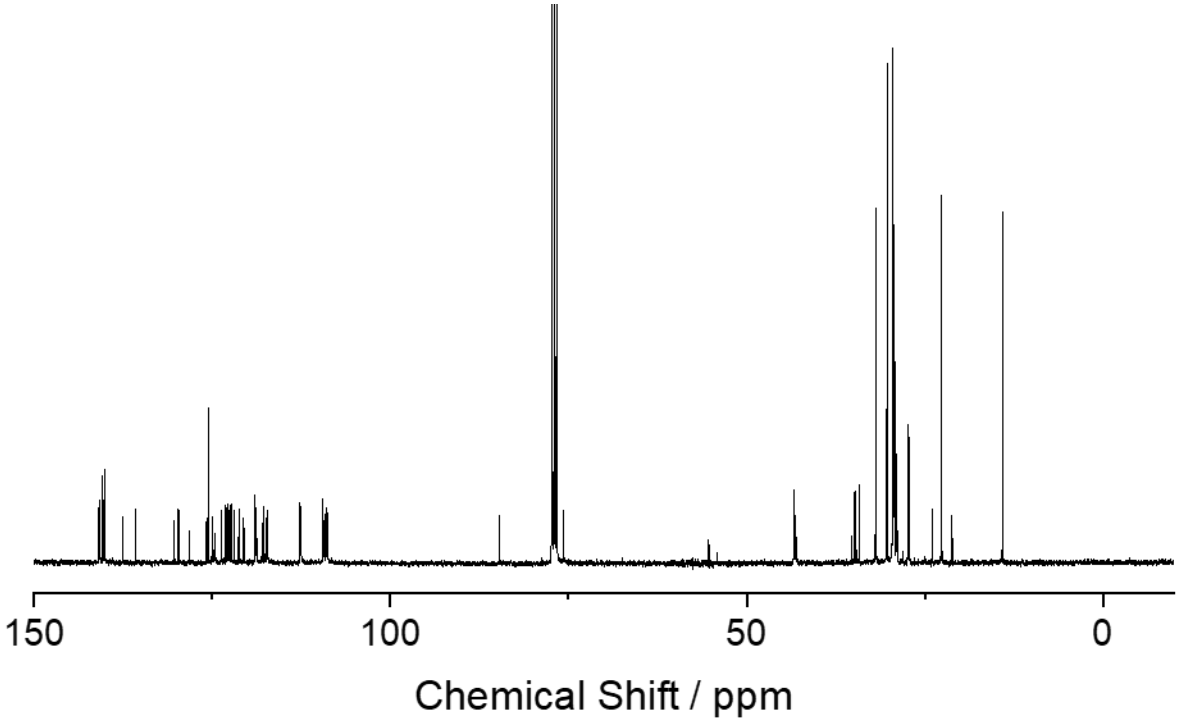
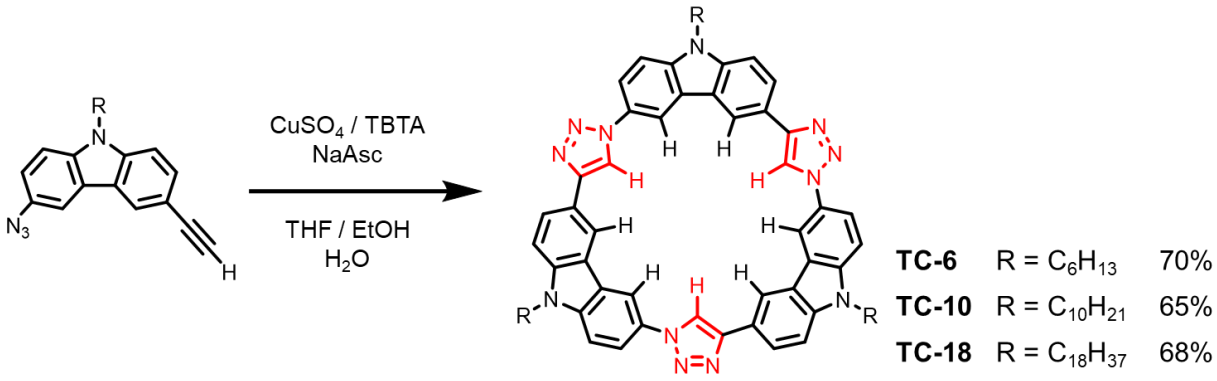


Figure S66. ^{13}C NMR spectrum of **trimer-6MeCy10**.

S5. General Synthesis and Characterization of Macrocycles

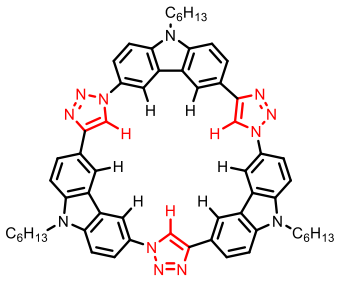


Scheme 4. The one-pot synthesis of a *C*$_3$-symmetric tricarb macrocycle.

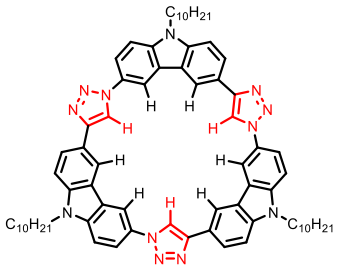
One-pot macrocyclization of difunctionalized carbazole building blocks – $CuSO_4 \cdot 5H_2O$, sodium ascorbate, and TBTA were dissolved in a 2:1:1 mixture of THF, ethanol, and water and degassed under argon for 15 minutes. A degassed solution of difunctional monomer **7** was dissolved in a 2:1 mixture of THF and ethanol and was added dropwise to the $CuSO_4$ solution over 6 h at 60 °C. The reaction mixture was stirred for an additional 2 h, then cooled to room temperature. Organic solvents (THF and ethanol) were removed in vacuo. The mixture was extracted with $CHCl_3$, and the organic phase was washed with NH_4Cl solution (1 M) and dried with $MgSO_4$, filtered, and concentrated in vacuo. The tricarb macrocycle was obtained following column chromatography.

Catalytic closing of the azido-alkylnyl-crescent trimer – Azido-alkynyl crescent **trimer** was dissolved in a 2:1:1 mixture of THF, ethanol, and H_2O and degassed with argon for 15 minutes. A solution of $CuSO_4 \cdot 5H_2O$, sodium ascorbate and TBTA in a 2:1:1 mixture of THF, ethanol, and water was then added to the degassed crescent solution. The reaction mixture was heated to 60 °C and stirred for 6 hours, then cooled to room temperature. The reaction was quenched by the addition of an aqueous solution of NH_4Cl (1 M) and the resulting mixture was extracted with three portions of $CHCl_3$. The organic phases were combined and dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting tricarb macrocycle was purified by column chromatography.

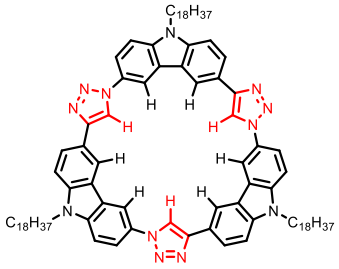
Thermal closing of the azido-alkylnyl-crescent trimer – A solution of azido-alkynyl crescent **trimer** in toluene was heated to 100 °C in a sealed vessel for 4 days with stirring. Toluene was then removed in vacuo and the tricarb macrocycle was purified by column chromatography.



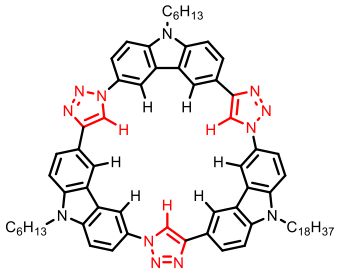
Trihexyl-tricarbazolo-triazolophane (TC-6) – TC-6 was synthesized following the general one-pot macrocyclization procedure from difunctional carbazole **7a** (0.94 g, 3 mmol, 1 equiv.), $CuSO_4 \bullet 5\ H_2O$ (75 mg, 0.3 mmol, 0.1 equiv.), TBTA (160 mg, 0.3 mmol, 0.1 equiv.), and sodium ascorbate (119 mg, 0.6 mmol, 0.2 equiv.). Crude **TC-6** was purified by column chromatography on silica gel with an elution gradient of chloroform to 95:5 chloroform:ethyl acetate (1.98 g, 2.1 mmol, 70%). The ^{1}H NMR spectrum was identical to previous reports.[S2]



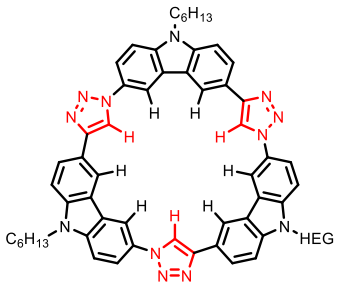
Tridecyl-tricarbazolo-triazolophane (TC-10) – TC-10 was synthesized following the general one-pot macrocyclization procedure from difunctional carbazole **7b** (1.12 g, 3 mmol, 1 equiv.), $CuSO_4$•5 H_2O (75 mg, 0.3 mmol, 0.1 equiv.), TBTA (160 mg, 0.3 mmol, 0.1 equiv.), and sodium ascorbate (119 mg, 0.6 mmol, 0.2 equiv.). Crude **TC-10** was purified by column chromatography on silica gel with an elution gradient of chloroform to 95:5 chloroform:ethyl acetate (2.18 g, 1.95 mmol, 65%). The ^{1}H NMR spectrum was identical to previous reports.[S3]



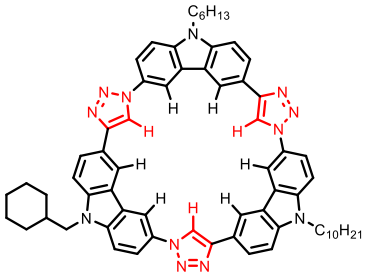
Trioctadecyl-tricarbazolo-triazolophane (TC-18) – TC-18 was synthesized following the general one-pot macrocyclization procedure from difunctional carbazole **7c** (1.45 g, 3 mmol, 1 equiv.), $CuSO_4$•5 H_2O (75 mg, 0.3 mmol, 0.1 equiv.), TBTA (160 mg, 0.3 mmol, 0.1 equiv.), and sodium ascorbate (119 mg, 0.6 mmol, 0.2 equiv.). Crude **TC-18** was purified by column chromatography on silica gel with an elution gradient of chloroform to 95:5 chloroform:ethyl acetate (3.20 g, 2 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.29 (s, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.7 Hz, 1H), 8.13 (s, 1H), 7.24 (d, J = 8.5 Hz, 2H), 4.16 (t, J = 7.4 Hz, 2H), 1.83 (dt, J = 13.7, 7.2 Hz, 2H), 1.46 – 1.18 (m, 30H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.63, 140.87, 139.97, 129.35, 123.99, 122.61, 122.5, 121.96, 118.39, 117.7, 117.48, 110.59, 109.45, 109.28, 43.23, 31.84, 29.63, 29.50, 29.48, 29.21, 29.35, 28.92, 27.19, 22.74, 22.30, 14.01 (six carbon peaks of the octadecyl chain are overlapping with others in the 30-29 ppm region). HRMS (ESI) calcd for $C_{96}H_{132}N_{12}$+PF_6: 1598.0345 $[M+PF_6]^-$; found: 1598.0359.



Dihexyl-octadecyl-tricarbazolo-triazolophane (TC-6618) – TC-6618 was synthesized following the general procedure for the catalytic closing of trimers from **trimer-6618** (1.20 g, 0.95 mmol, 1 equiv.), $CuSO_4$•5 H_2O (3 mg, 0.09 mmol, 0.1 equiv.), TBTA (6 mg, 0.09 mmol, 0.1 equiv.), and sodium ascorbate (11 mg, 0.18 mmol, 0.2 equiv.). Crude **TC-6618** was purified by column chromatography on silica gel with an elution gradient of chloroform to 95:5 chloroform:ethyl acetate (883 mg, 0.7 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.30 (s, 1H), 8.21 (d, J = 6.6 Hz, 1H), 8.17 (d, J = 7.3 Hz, 1H), 8.14 (s, 1H), 7.24 (d, J = 6.7 Hz, 2H), 4.16 (t, J = 5.9 Hz, 2H), 1.83 (p, J = 5.4 Hz, 2H), 1.49 – 1.12 (m, 30H), 0.90 (t, J = 5.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.65, 149.64, 140.87, 139.93, 129.33, 123.94, 122.57, 122.47, 121.90, 118.34, 117.74, 117.53, 110.62, 109.39, 109.33, 43.37, 34.11, 31.96, 31.54, 29.81, 29.80, 29.70, 29.66, 29.56, 29.55, 29.48, 29.37, 29.34, 29.20, 29.18, 27.34, 26.97, 26.92, 22.69, 22.61, 14.13, 13.98. HRMS (ESI) calcd for $C_{72}H_{84}N_{12}$+PF_6: 1261.6589 $[M+PF_6]^-$; found: 1261.6598.



Dihexyl-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-tricarbazolo-triazolophane (TC-66HEG) – TC-66HEG was synthesized following the general procedure for the catalytic closing of trimers from **trimer-66HEG** (1.16 g, 0.9 mmol, 1 equiv.), $CuSO_4$•5 H_2O (3 mg, 0.09 mmol, 0.1 equiv.), TBTA (6 mg, 0.09 mmol, 0.1 equiv.), and sodium ascorbate (11 mg, 0.18 mmol, 0.2 equiv.). Crude **TC-6618** was purified by column chromatography on silica gel with an elution gradient of chloroform to 4:1 chloroform:ethyl acetate (770 mg, 0.6 mmol, 70%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.30 (s, 1H), 8.21 (d, J = 6.6 Hz, 1H), 8.17 (d, J = 7.3 Hz, 1H), 8.14 (s, 1H), 7.24 (d, J = 6.7 Hz, 2H), 4.55 (t, J = 3.6 Hz, 2H), 4.35 (t, J = 5.1 Hz, 4H), 3.92 (t, J = 3.4 Hz, 2H), 3.77 – 3.43 (m, 20H), 3.36 (s, 3H), 2.08 – 1.79 (m, 4H), 1.44 – 1.20 (m, 12H), 0.90 (dt, J = 7.9, 4.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.65, 140.85, 140.00, 129.25, 124.09, 122.55, 122.51, 122.01, 118.42, 117.69, 117.55,110.60, 109.46, 109.31, 72.01, 70.90, 70.65, 70.58, 70.56, 69.31, 58.99, 43.79, 43.56, 43.33, 31.84, 31.70, 29.80, 29.70, 29.68, 29.63, 29.61, 29.44, 29.27, 29.07, 28.98, 27.28, 27.27, 26.95, 22.79, 22.47, 14.07, 14.05. HRMS (ESI) calcd for $C_{67}H_{74}N_{12}O_6$+PF_6: 1287.5502 $[M+PF_6]^-$; found: 1287.5532.



Hexyl-methylcyclohexyl-decyl-tricarbazolo-triazolophane (TC-610MeCy) – TC-610MeCy was synthesized following the general procedure for the catalytic closing of trimers from **trimer-6MeCy10** (1.10 g, 0.95 mmol, 1 equiv.), $CuSO_4$•5 H_2O (3 mg, 0.09 mmol, 0.1 equiv.), TBTA (6 mg, 0.09 mmol, 0.1 equiv.), and sodium ascorbate (11 mg, 0.18 mmol, 0.2 equiv.). Crude **TC-6618** was purified by column chromatography on silica gel with an elution gradient of chloroform to 95:5 chloroform:ethyl acetate (810 mg, 0.7 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 3H), 8.29 (s, 3H), 8.25 – 8.09 (m, 6H), 7.25 (d, J = 7.2 Hz, 6H), 4.17 (t, J = 5.5 Hz, 4H), 3.99 (d, J = 5.8 Hz, 2H), 2.01 – 1.89 (m, 1H), 1.83 (p, J = 11.9, 5.9 Hz, 4H), 1.75 – 1.64 (m, peaks partially overlap with residual water peak), 1.46 – 1.22 (m, 20H), 1.21 – 1.09 (m, 5H), 0.99 – 0.81 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.78, 140.88, 139.98, 129.29, 123.98, 122.57, 122.41, 121.96, 118.30, 117.66, 117.62, 110.63, 109.52, 109.31, 49.81, 43.40, 38.36, 34.17, 31.94, 31.57, 31.27, 30.35, 29.64, 29.53, 29.48, 29.40, 29.21, 29.20, 28.83, 27.19, 26.89, 26.17, 25.79, 25.74, 22.65, 22.59, 14.05, 13.96. HRMS (ESI) calcd for $C_{65}H_{68}N_{12}$+PF_6: 1161.5337 $[M+PF_6]^-$; found: 1161.5341.

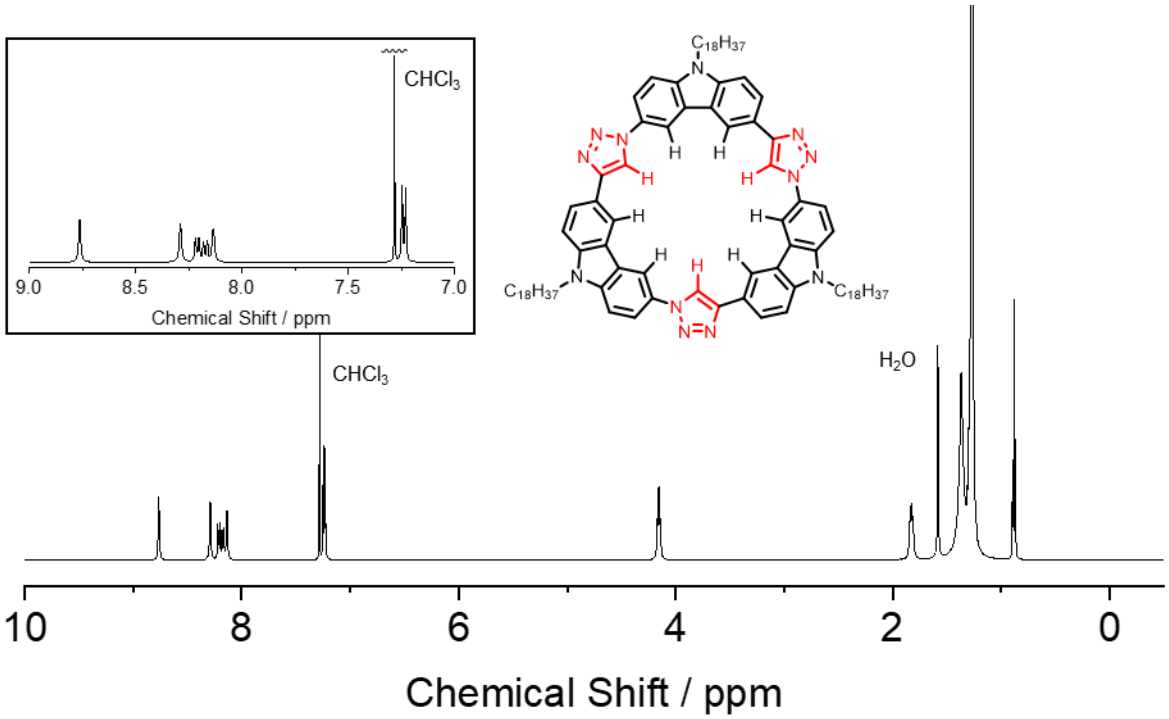


Figure S67. ^{1}H NMR spectrum of **TC-18**.

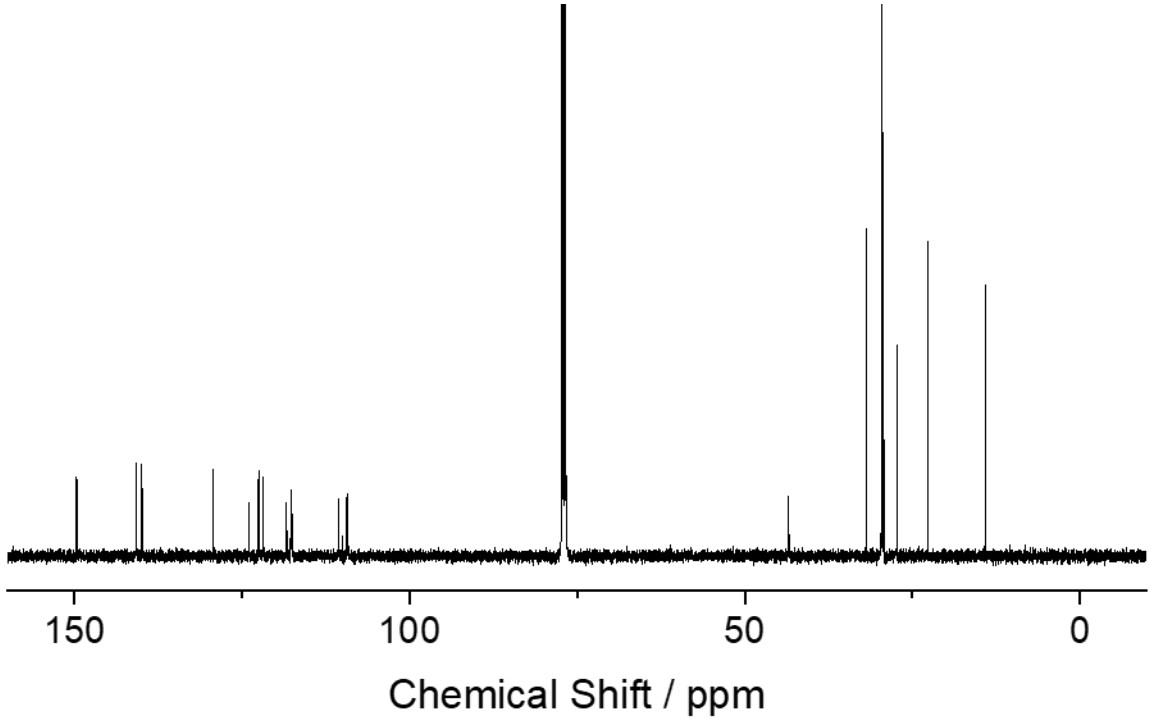


Figure S68. ^{13}C NMR spectrum of **TC-18**.

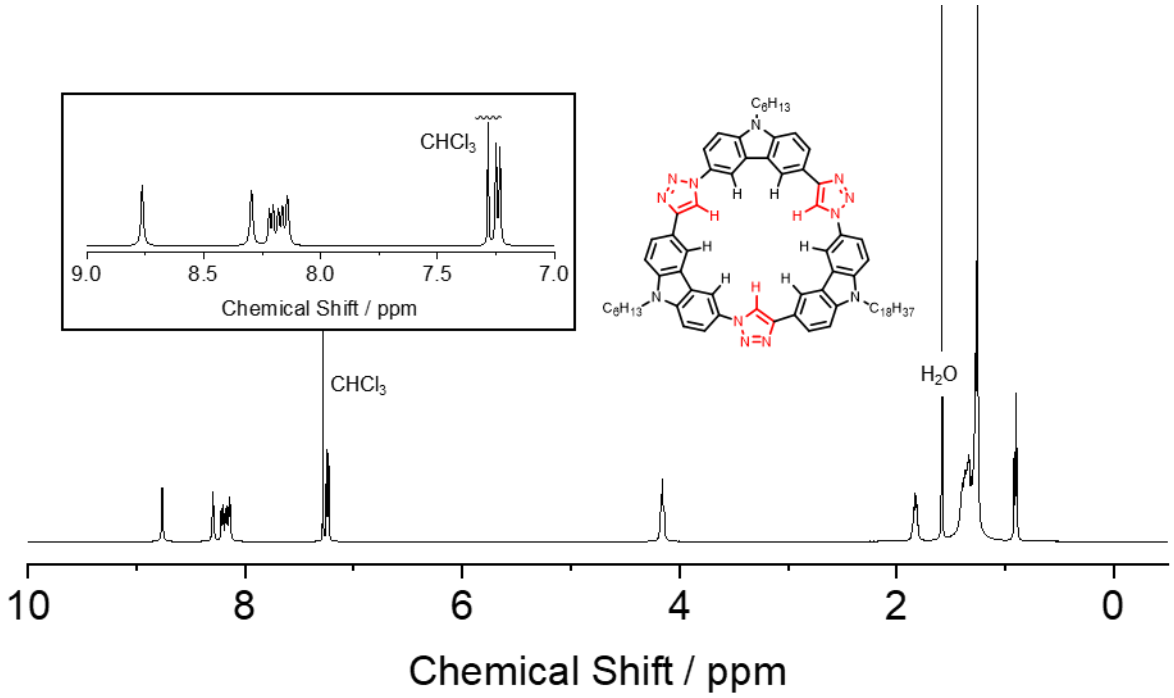


Figure S69. ^{1}H NMR spectrum of **TC-6618**.

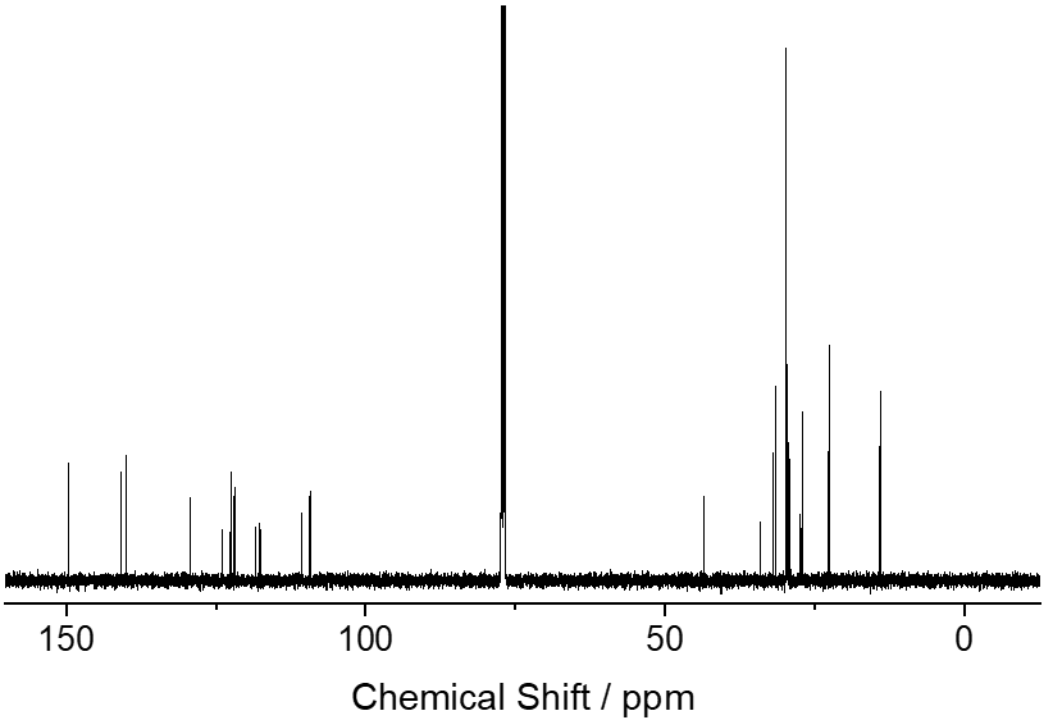


Figure S70. ^{13}C NMR spectrum of **TC-6618**.

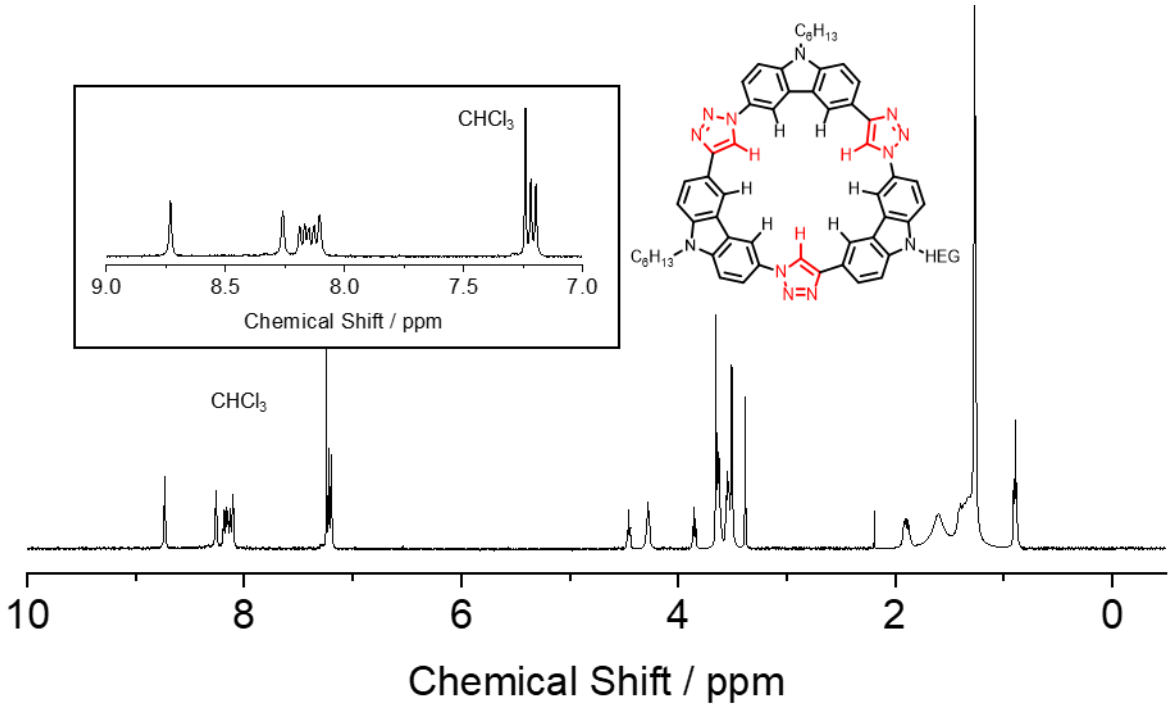


Figure S71. ^{1}H NMR spectrum of **TC-66HEG**.

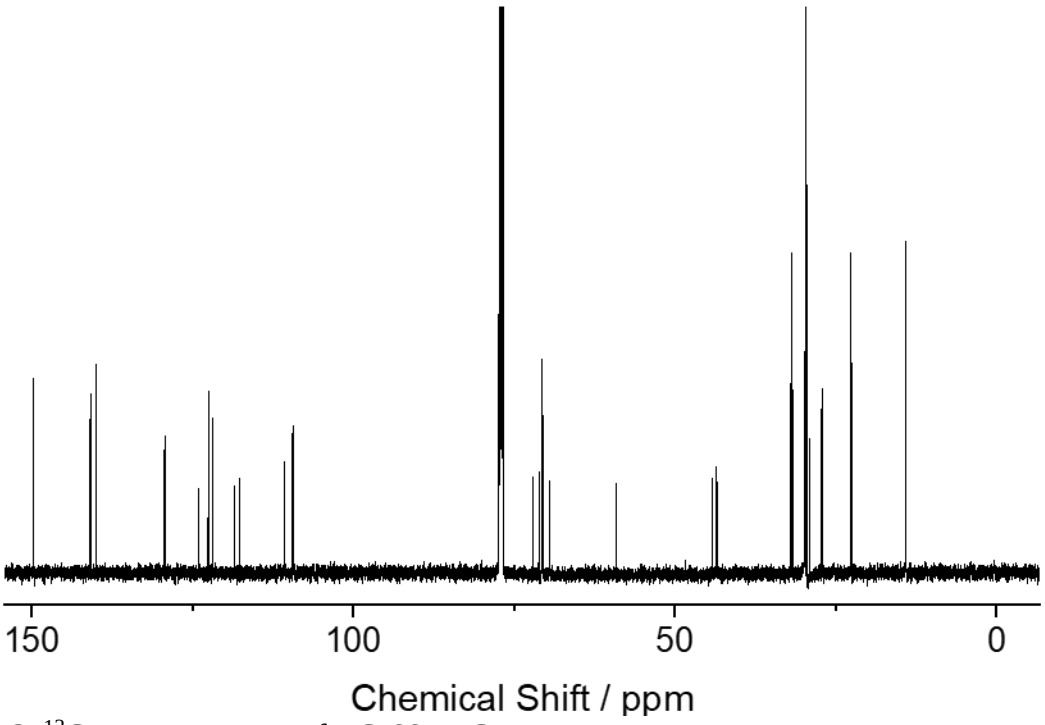


Figure S72. ^{13}C NMR spectrum of **TC-66HEG**.

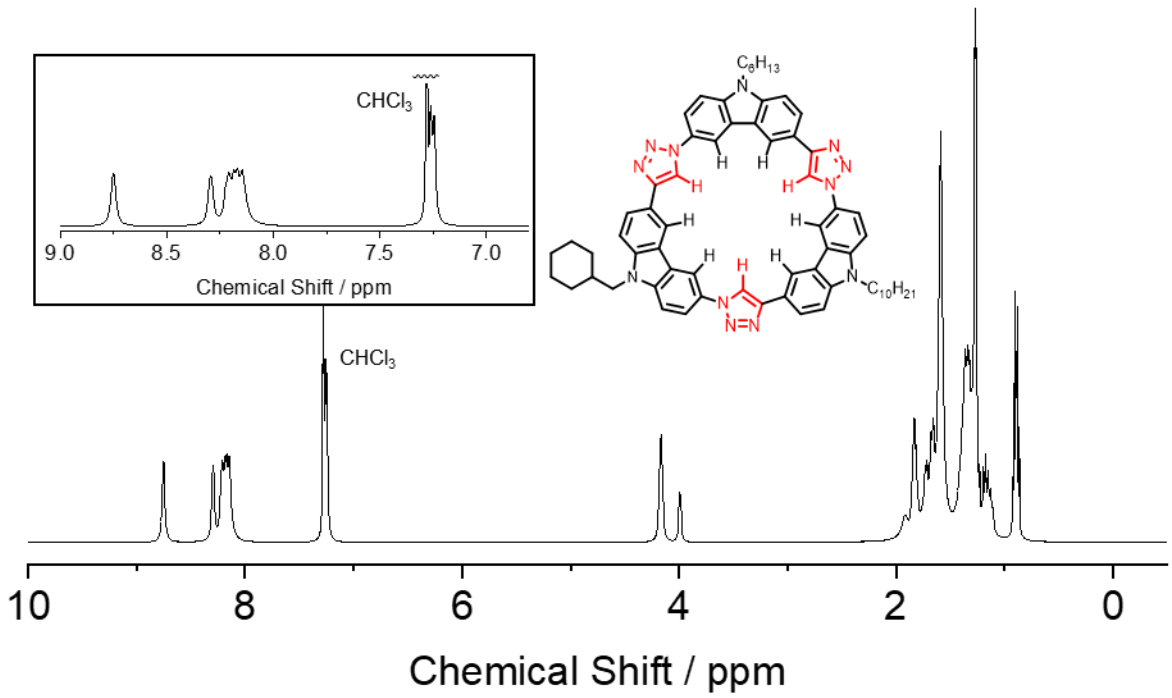


Figure S73. ^{1}H NMR spectrum of **TC-610MeCy**.

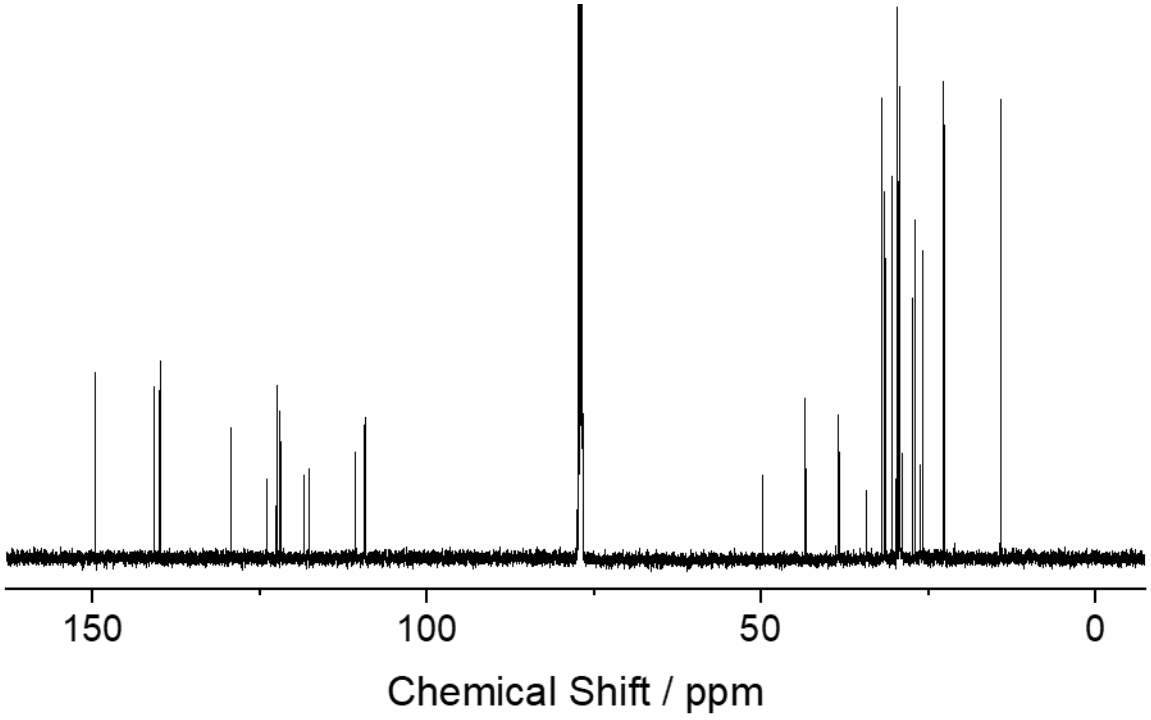


Figure S74. ^{13}C NMR spectrum of **TC-610MeCy**.

S6. Additional STM Images and Characterization

Table S1: The observed surface polymorphs of tricarb macrocycles.

	Flower	*Gap*	*Honeycomb*	*Non-ordered*
TC-6			✓	✓
TC-10	✓		✓	
TC-18	✓		✓	
TC-6618		✓	✓	✓
TC-66HEG			✓	✓
TC-610MeCy			✓	✓

Table S2: Unit cell parameters for the ordered surface polymorphs of tricarb macrocycles studied.

		α (nm)	*β (nm)*	*γ (deg.)*
Flower	**TC-10**[a]	5.34 ± 0.11	5.34 ± 0.11	60 ± 1
	TC-18[c]	5.37 ± 0.07	5.37 ± 0.07	60 ± 1
Gap Zig-zag	**TC-6618**[b]	3.96 ± 0.02	2.88 ± .02	60 ± 1
Gap Honeycomb	**TC-6618**[b]	5.97 ± 0.03	2.88 ± 0.02	81 ± 1
Honeycomb	**TC-6**[c]	2.92 ± 0.05	2.92 ± 0.05	60 ± 2
	TC-10[a]	2.89 ± 0.09	2.89 ± 0.09	60 ± 1
	TC-18[c]	2.92 ± 0.08	2.92 ± 0.08	60 ± 2
	TC-6618[c]	2.94 ± 0.07	2.94 ± 0.07	60 ± 2
	TC-66HEG[c]	2.92 ± 0.05	2.92 ± 0.05	61 ± 1
	TC-610MeCy[c]	2.94 ± 0.08	2.94 ± 0.08	59 ± 3

[a]Values were obtained from reference S3.
[b]Values were calculated from three independently measured, HOPG corrected images.
[c]Values were calculated from 10 independently measured, uncorrected images.

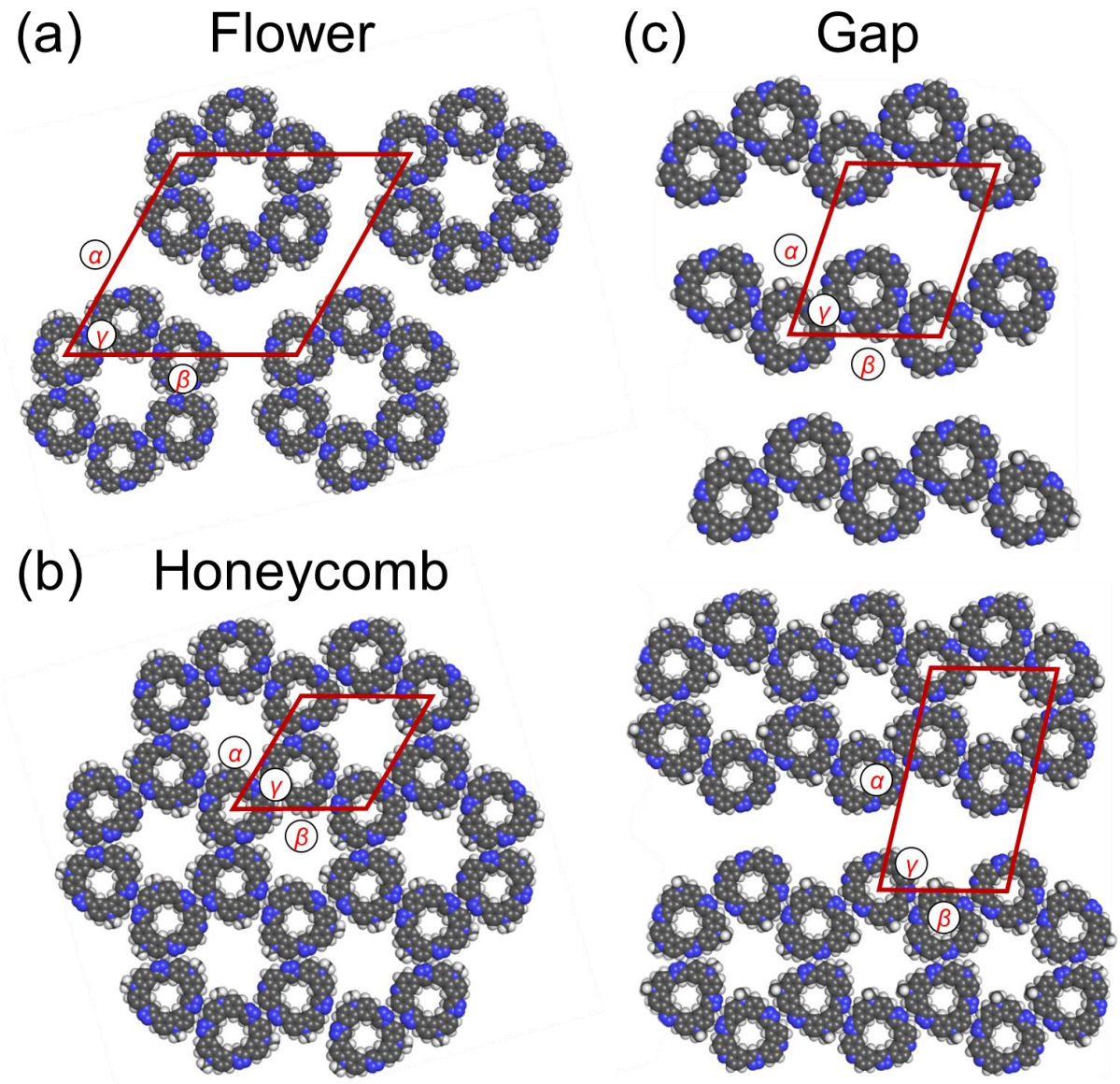


Figure S75. Molecular models and unit cells of the (a) flower, (b) honeycomb, and (c) gap phases.

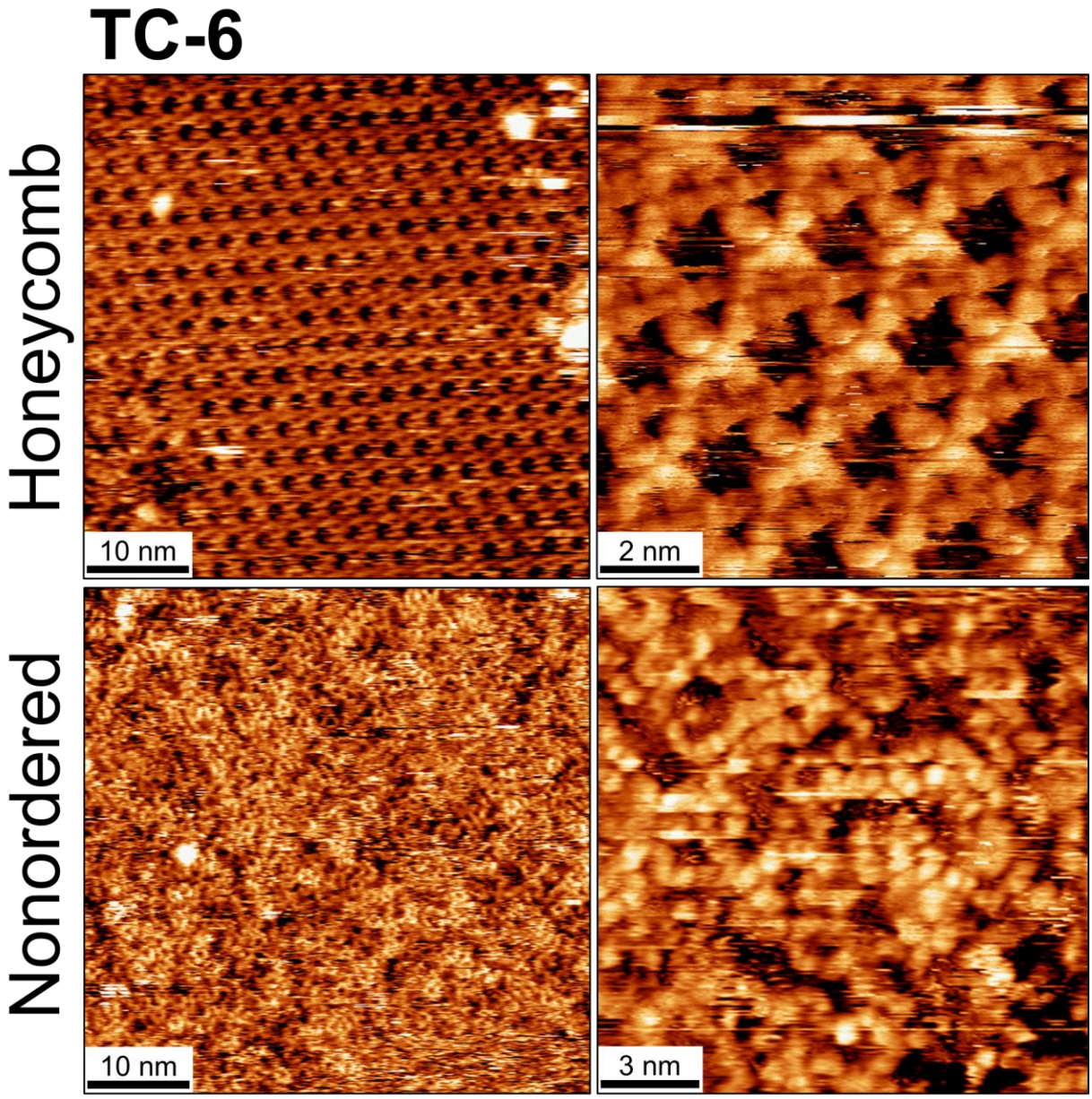


Figure S76. STM images of the surface polymorphs formed by the **TC-6** macrocycle: honeycomb (top row, 2.5 μM, I_t = 0.15 nA, V_{sample} = –1 V) and nonordered assembly (bottom row, 25 μM, I_t = 0.2 nA, V_{sample} = –0.8 V).

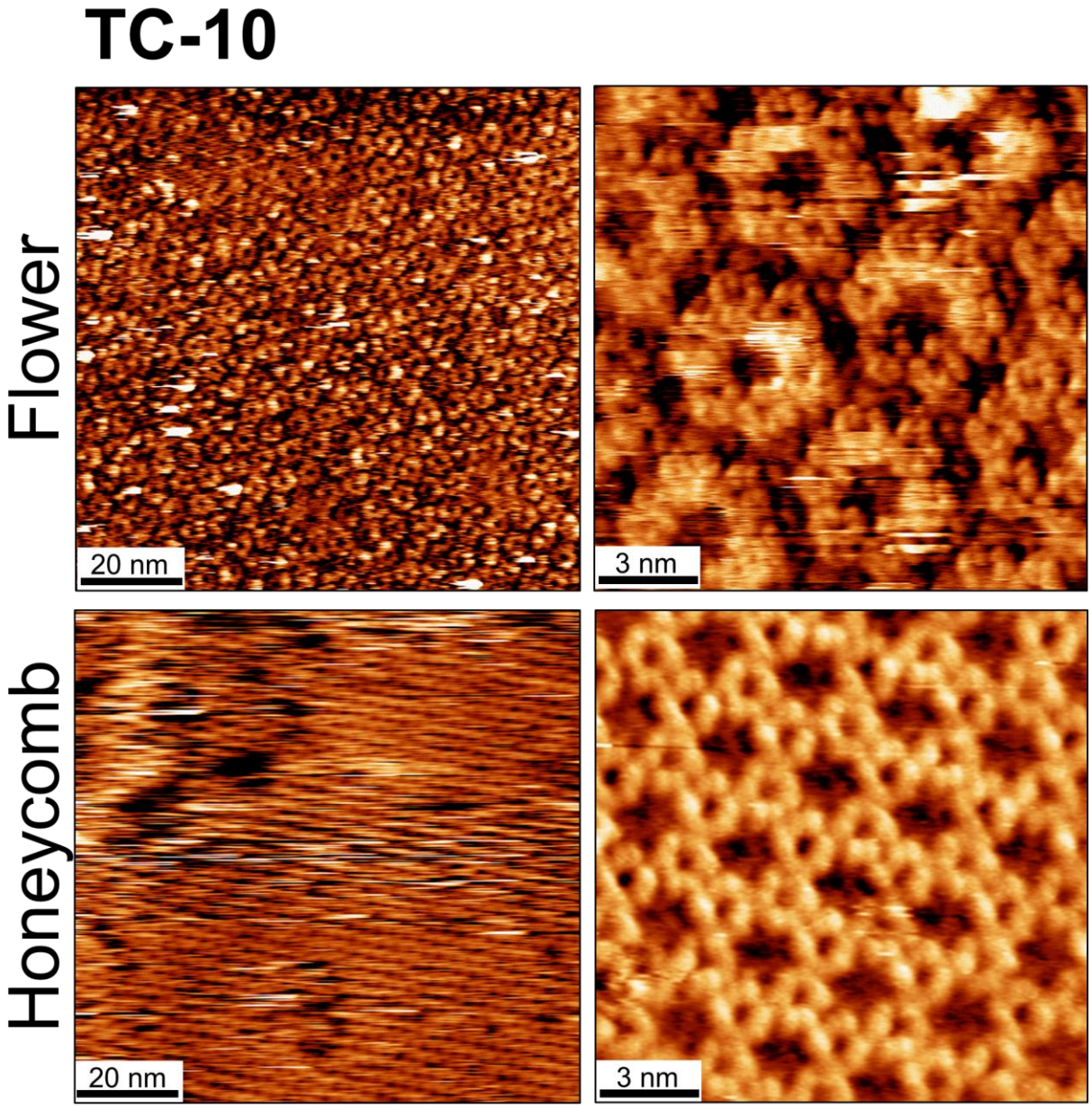


Figure S77. STM images of the surface polymorphs formed by the **TC-10** macrocycle: flower (top row, 75 μM, I_t = 0.03 nA, V_{sample} = –0.3 V) and honeycomb assembly (bottom row, 150 μM, I_t = 0.02 nA, V_{sample} = –0.3 V).

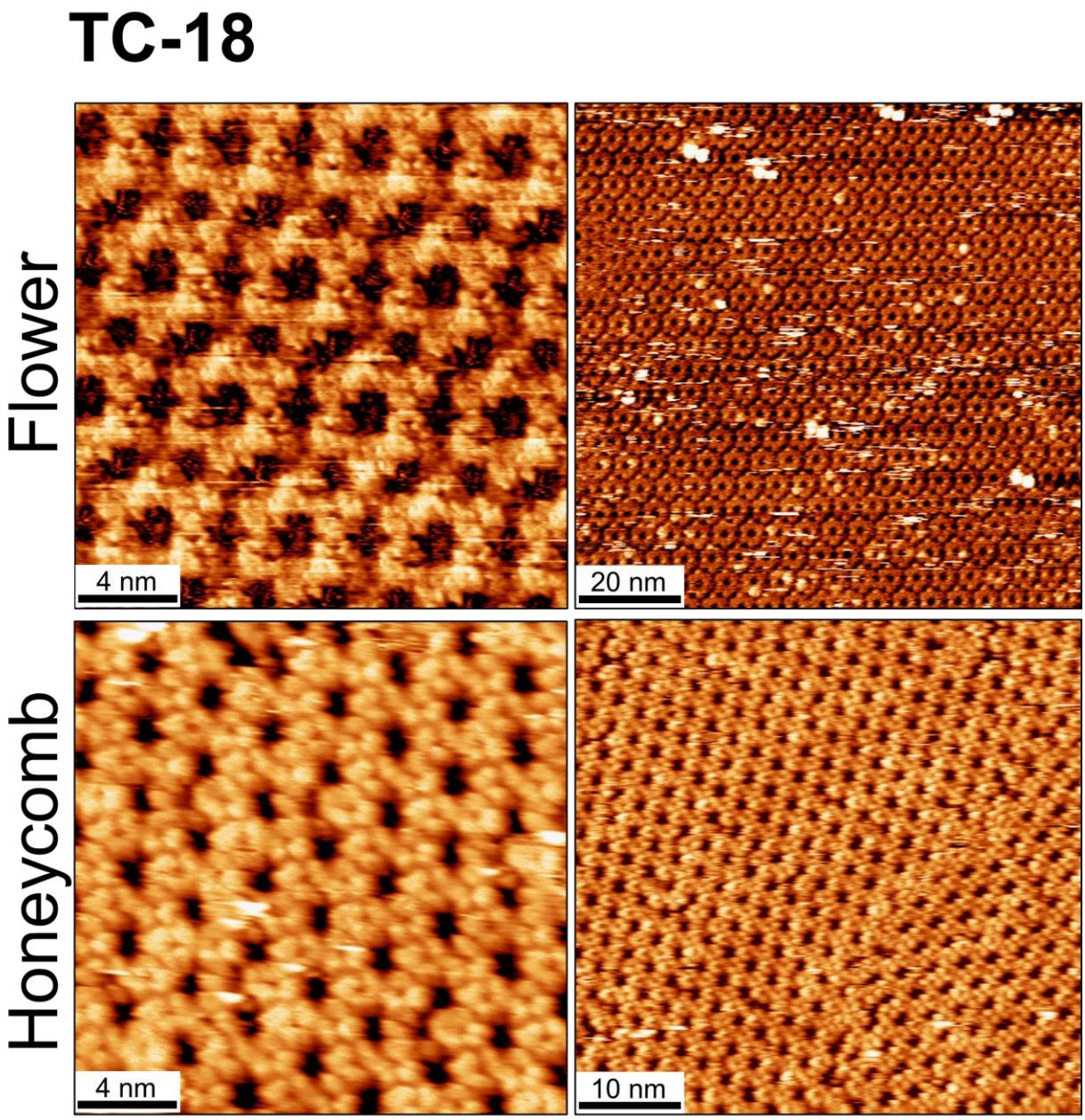


Figure S78. STM images of the surface polymorphs formed by the **TC-18** macrocycle: flower (top row, 5 μM, I_t = 0.3 nA, V_{sample} = –0.8 V) and honeycomb assembly (bottom row, 100 μM, I_t = 0.03 nA, V_{sample} = –0.4 V).

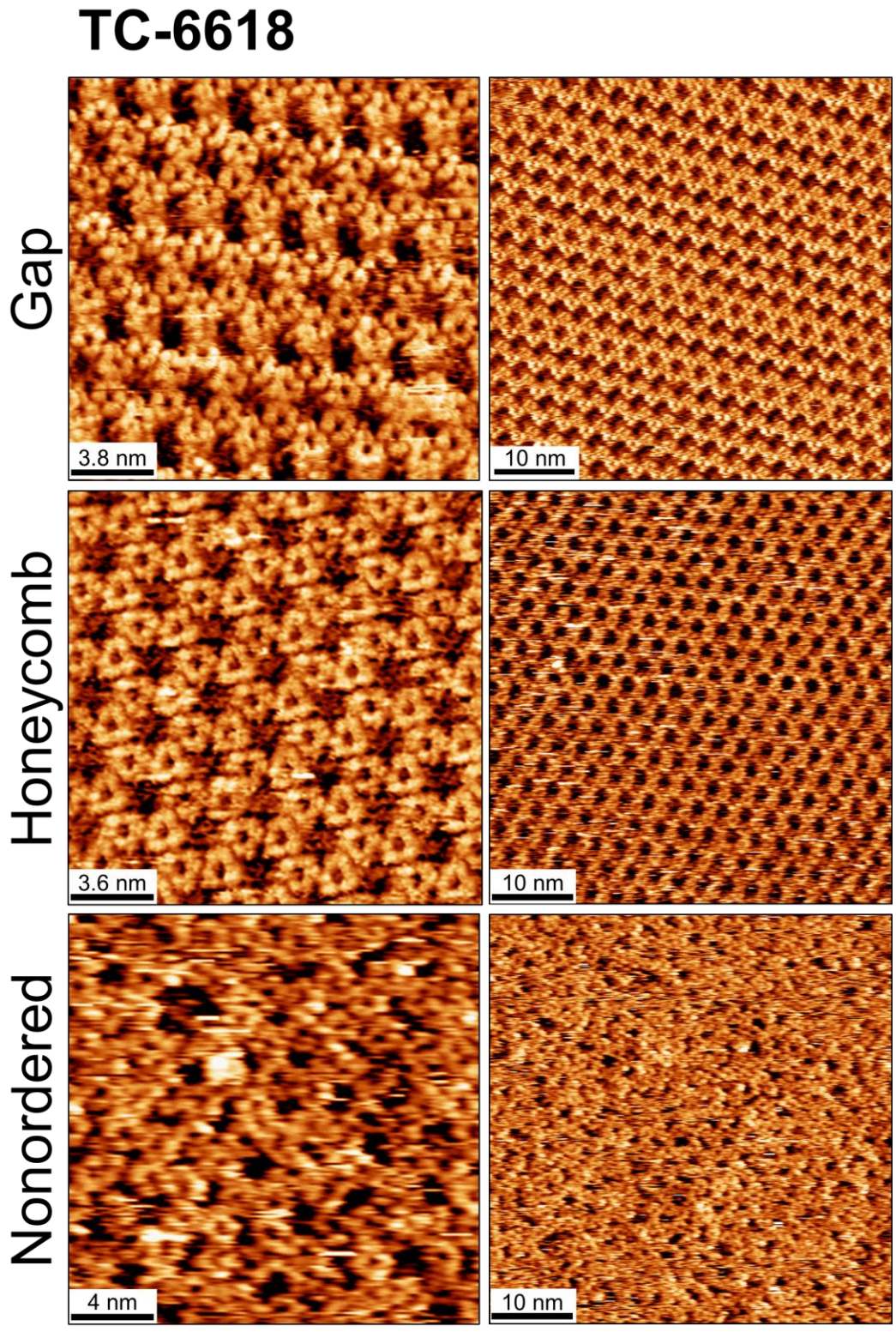


Figure S79. STM images of the surface polymorphs formed by the **TC-6618** macrocycle: gap (top row, 5 μM, I_t = 0.2 nA, V_{sample} = –0.8 V), honeycomb (middle row, 100 μM, I_t = 0.55 nA, V_{sample} = –1 V), and nonordered assemblies (bottom row, 300 μM, I_t = 0.5 nA, V_{sample} = –0.8 V).

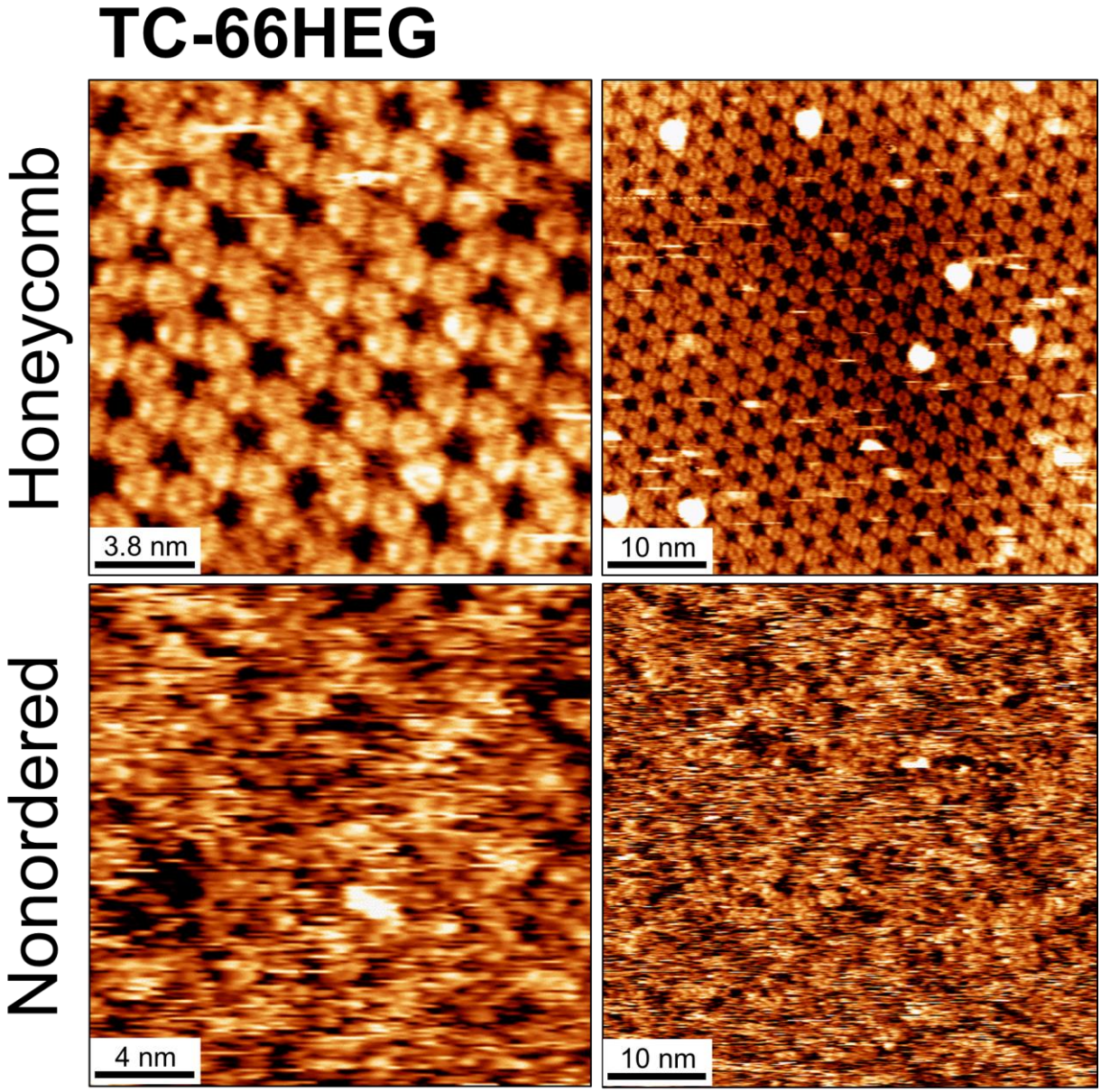


Figure S80. STM images of the surface polymorphs formed by the **TC-66HEG** macrocycle: honeycomb (top row, 5 μM, I_t = 0.3 nA, V_{sample} = –0.8 V) and nonordered assembly (bottom row, 1000 μM, I_t = 1 nA, V_{sample} = –0.7 V).

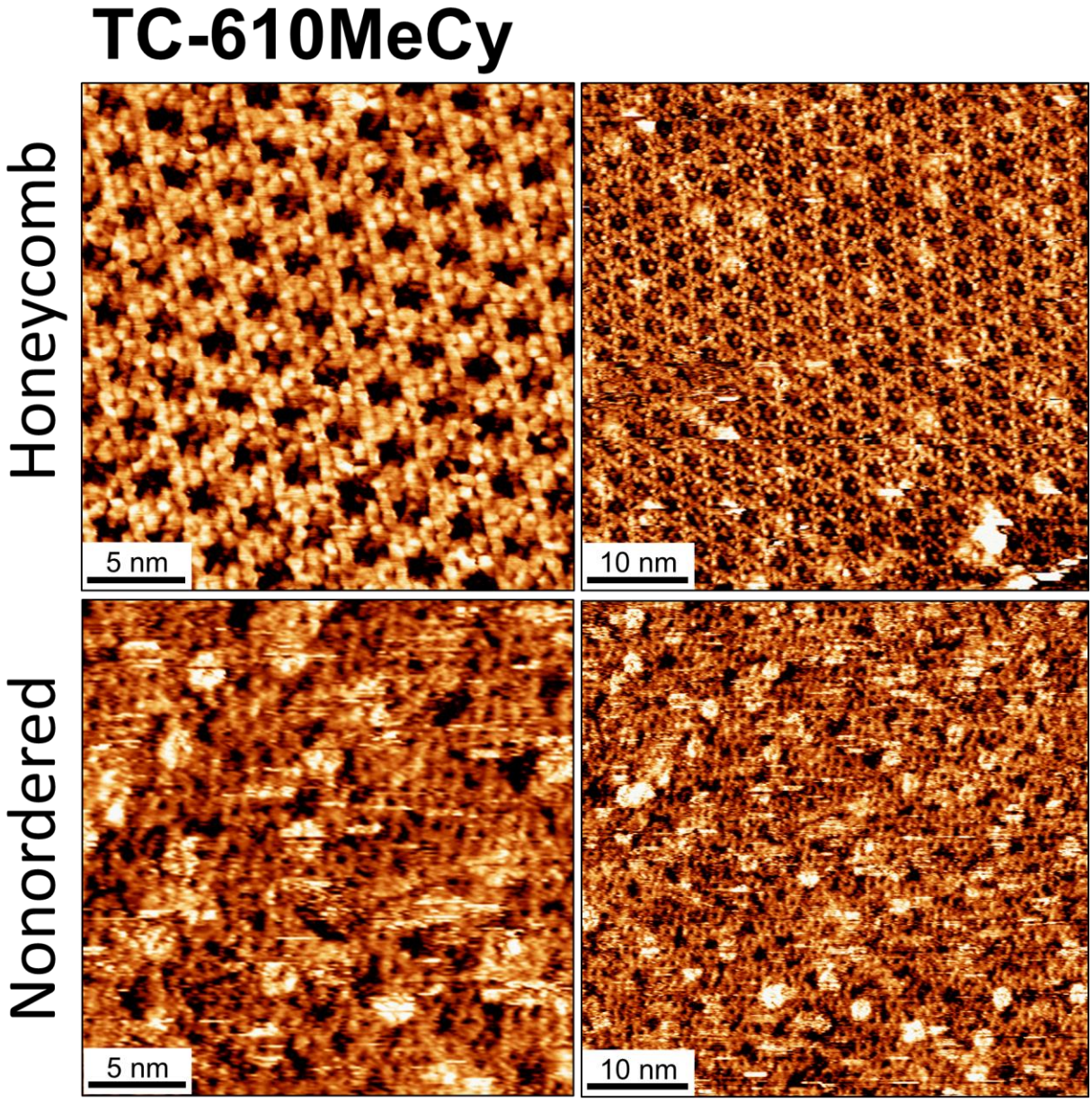


Figure S81. STM images of the surface polymorphs formed by the **TC-610MeCy** macrocycle: honeycomb (top row, 10 μM, I_t = 0.15 nA, V_{sample} = –0.7 V) and nonordered assembly (bottom row, 300 μM, I_t = 1.1 nA, V_{sample} = –0.6 V).

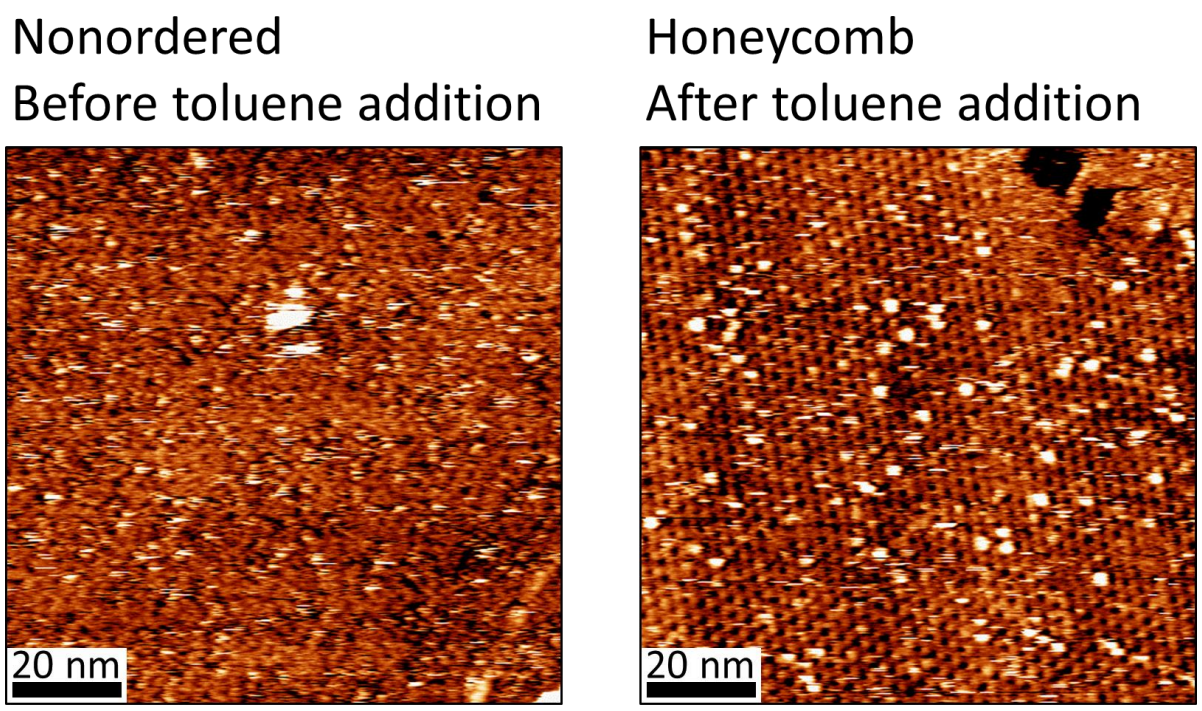


Figure S82. STM images of **TC-610MeCy** before and after *in situ* toluene addition. Left: before the addition of toluene, only disordered is observed (1000 μM, I_t = 2.3 nA, V_{sample} = –0.7 V). Right: after 16 μL of toluene have been added *in situ* to the sample and after subsequent evaporation of toluene (final **tricarb** conc.: 1000 μM, I_t = 0.4 nA, V_{sample} = –0.7 V). Most of the surface is now covered with honeycomb even though the final sample concentration is still 1000 μM.

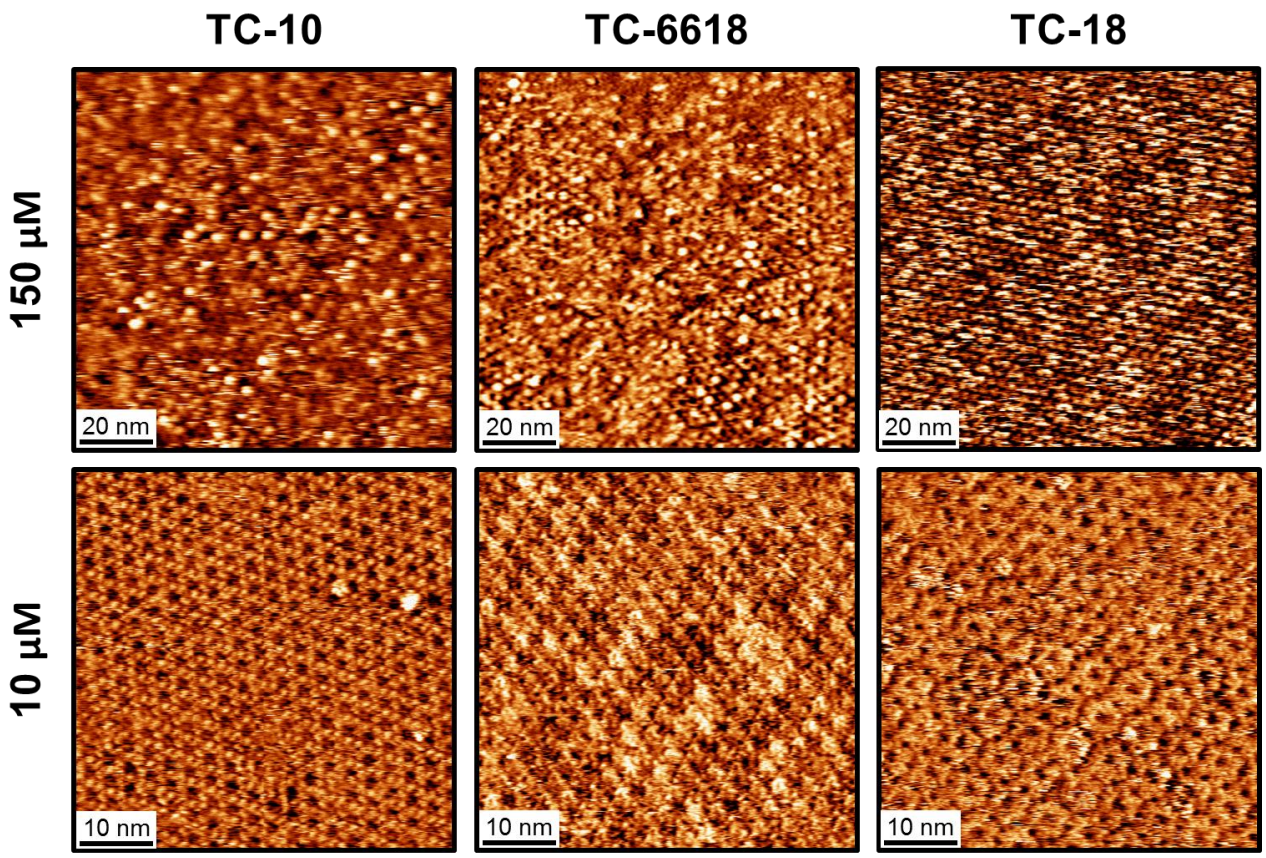


Figure S83. STM images of **TC-10**, **TC-6618**, and **TC-18** at 150 µM and 10 µM concentrations. Stacking of tricarb molecules perpendicular to the surface was observed for all tricarb species, and higher concentrations of tricarb solutions produced more stacking. However, the formation of full multilayers were never observed at any concentration with any tricarb species. Low bias ($V_{sample} \geq$ –0.4 V) was optimal for STM imaging of stacking which differed from optimal STM imaging 2D tricarb self-assemblies ($V_{sample} \leq$ –0.7 V). Conditions: I_t = 0.05 to 0.10 nA, V_{sample} = –0.4 V.

S7. References

S1. Sodium Azide. In *Encyclopedia of Reagents for Organic Synthesis*.

S2. Dobscha, J. R.; Debnath, S.; Fadler, R. E.; Fatila, E. M.; Pink, M.; Raghavachari, K.; Flood, A. H., Host–Host Interactions Control Self-assembly and Switching of Triple and Double Decker Stacks of Tricarbazole Macrocycles Co-assembled with anti-Electrostatic Bisulfate Dimers. *Chem. Eur. J.* **2018**, *24*, 9841-9852.

S3. Lee, S.; Hirsch, B. E.; Liu, Y.; Dobscha, J. R.; Burke, D. W.; Tait, S. L.; Flood, A. H., Multifunctional Tricarbazolo Triazolophane Macrocycles: One-Pot Preparation, Anion Binding, and Hierarchical Self-Organization of Multilayers. *Chem. Eur. J.* **2016**, *22*, 560-569.