

Supporting Information for:

**Macrocyclic Depolymerization of Arylene-Ethynylene Copolymers:
A Dynamic Combinatorial Method**

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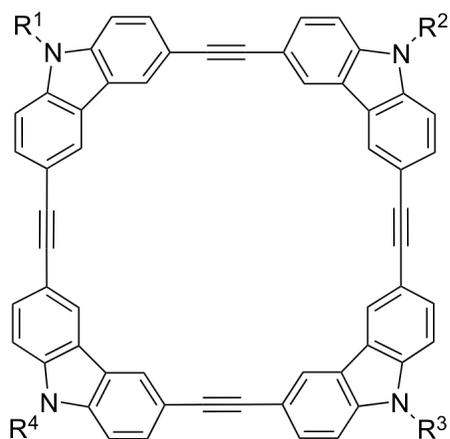
General. All air or moisture-sensitive manipulations were performed under an atmosphere of argon using standard Schlenk techniques or in an argon filled glove box. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 precoated silica gel plates. Visualization was performed with UV light (254 nm) or iodine stain. Flash chromatography was performed using 60 Å silica gel from Silicycle, Inc. All polymerization and metathesis reactions were prepared in an argon-filled glove box and run under an inert atmosphere. The reaction vessels used, unless otherwise specified, were 20 mL vials fitted with PTFE/silicone septa. All glassware was oven-dried before use.

Materials. Unless otherwise stated, all starting materials and reagents were purchased from commercial sources and used without further purification. Carbazole (Acros 96%), CuI (99.999%, PURATREM grade, Strem), piperidine (Aldrich, redistilled 99.5%), N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from a Solvent Delivery System (SDS) equipped with activated neutral alumina columns. Triethylamine was freshly distilled from CaH₂ under a nitrogen atmosphere. CCl₄ was distilled over P₂O₅ and degassed before use.

Characterization. ¹H and ¹³C NMR spectra were obtained on Varian Unity 400, Unity 500, and VXR 500 spectrometers. Chemical shifts are reported in δ (ppm) relative to the residual solvent protons (CDCl₃: 7.26 for ¹H, 77.0 for ¹³C). Coupling constants (J) are expressed in hertz (Hz). Splitting patterns are designated as s (singlet); d (doublet); t (triplet); dd (doublet of doublets); td (triplet of doublets); m (multiplet). Low resolution ESI mass spectra were recorded on a Waters Quattro II spectrometer. High resolution ESI mass spectra were recorded on a Micromass Q-Tof Ultima spectrometer. MALDI mass spectra were recorded on an Applied Biosystems Voyager-DE STR spectrometer. MALDI analysis of macrocycles was carried out using the dithranol matrix. Analytical gel permeation chromatography (GPC) analyses were performed on a system composed of a Waters 515 HPLC pump, a Thermostations Trace series AS100 autosampler, a series of three Waters HR Styragel columns (7.8 × 300 mm, HR3, HR4, and HR5), and a Viscotek TDA Model 300 triple detector array, in HPLC grade THF (flow rate = 1.0 mL/min) at 30 °C. The GPC was calibrated using a series of monodisperse polystyrene standards.

Synthesis of Carbazolyl-ethynylene Copolymers and Macrocycles

Polymer (5) from 3 and 4. In an argon filled glovebox an oven dried vial was loaded with **4**¹ (705 mg, 1.26 mmol, 1 equiv.), **3**² (450 mg, 1.25 mmol, 1 equiv.), Pd(PPh₃)₄ (60 mg, 0.052 mmol, 0.042 equiv.), CuI (4 mg, 0.021 mmol, 0.016 equiv.), dry THF (10 mL) and piperidine (3 mL). The mixture was sealed, removed from the box and heated at 60 °C for 48 hrs. The reaction was then cooled and poured into a flask containing MeOH (200 mL) to precipitate the polymer. The solid was collected by filtration and dried in vacuo to yield 689 mg of polymer **3c**. GPC (THF): Mn = 6700 g/mol, Mw = 12000 g/mol, PDI = 1.8, ret. time = 30.4 min.)



- 6a**, R¹, R², R³, R⁴ = C₁₀H₂₁
6b, R¹ = Tg; R², R³, R⁴ = C₁₀H₂₁
6c, R¹, R² = Tg; R³, R⁴ = C₁₀H₂₁
6d, R¹, R³ = Tg; R², R⁴ = C₁₀H₂₁
6e, R¹, R², R³ = Tg; R⁴ = C₁₀H₂₁
1b, R¹, R², R³, R⁴ = Tg

Macrocycles (1b and 6) from Polymer (5). In an argon filled glovebox an oven dried vial was loaded with molybdenum catalyst³ (40 mg, 0.06 mmol, 6.3 wt%), Ph₃SiOH (100 mg, 0.36 mmol, 15.9 wt%), and 1,2,4-trichlorobenzene (14 mL). The orange-brown solution was stirred for 5 minutes then polymer **5** (630 mg) was added. The vial was sealed, removed from the box and heated at 50 °C for 24 hrs. Multiple products were observed by TLC in DCM:Hexanes (2:1). The 1,2,4-trichlorobenzene was removed by vacuum distillation. GPC for the crude reaction mixture (THF): Mn = 1700 g/mol, Mw = 1700 g/mol, PDI = 1.0, ret. time = 35.3 min.). The products were purified by silica gel column chromatography eluting with 0-5% MeOH in chloroform. Separation yielded **6a** (27 mg, 4.3%), mixture **6b-d** (325 mg, 52%), **6e** (89 mg, 14%), and **1b** (38 mg, 6.0%). The mixture of **6b-d** was further purified by silica gel column chromatography eluting with DCM:chloroform:MeOH (49.5:49.5:1 v/v) to yield **6c-d** (97 mg, 15%) and **6b** (72 mg, 11%). GPC for crude reaction mixture (THF): Mn = 1700 g/mol, Mw = 1700 g/mol, PDI = 1.0, ret. time = 35.3 min.)

NMR Data for **1b** and **6**

1b – Data matched that of the product obtained from the depolymerization.²

6a¹H NMR (500 MHz, CDCl₃): δ 8.42 (s, 8H, ArH), 7.71 (dd, J = 1.5, 8.5 Hz, 8H, ArH), 7.39 (d, J = 8.5 Hz, 8H, ArH), 4.31 (t, J = 7.2 Hz, 8H, NCH₂), 1.92-1.89 (m, 8H, CH₂), 1.43-1.22 (m, 56H, CH₂), 0.88 (t, J = 7.0 Hz, 12H, CH₃).

6b¹H NMR (500 MHz, CDCl₃): δ 8.43-8.41 (m, 8H, ArH), 7.72-7.71 (m, 8H, ArH), 7.46 (d, J = 8.5 Hz, 2H, ArH), 7.39 (d, J = 8.5 Hz, 6H, ArH), 4.52 (t, J = 5.75 Hz, 2H, NCH₂CH₂O), 4.31 (t, J

= 7.25 Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.92 (t, $J = 5.75$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.57-3.43 (m, 8H, OCH_2), 3.36 (s, 3H, OCH_3), 1.92-1.89 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.42-1.26 (m, 42H, CH_2), 0.88 (t, $J = 7.0$ Hz, 9H, CH_2CH_3).

6c-d ^1H NMR (500 MHz, CDCl_3): δ 8.40-8.39 (m, 8H, ArH), 7.72-7.70 (m, 8H, ArH), 7.45 (d, $J = 8.5$ Hz, 4H, ArH), 7.38 (d, $J = 8.5$ Hz, 4H, ArH), 4.51 (t, $J = 5.75$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 4.30 (t, $J = 7.25$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.91 (t, $J = 5.75$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.57-3.43 (m, 16H, CH_2), 3.35 (s, 6H, OCH_3), 1.91-1.88 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.42-1.22 (m, 28H, CH_2), 0.88 (t, $J = 7.0$ Hz, 6H, CH_2CH_3).

6e ^1H NMR (500 MHz, CDCl_3): δ 8.34-8.32 (m, 8H, ArH), 7.70-7.69 (m, 8H, ArH), 7.42 (d, $J = 8.5$ Hz, 6H, ArH), 7.36 (d, $J = 8.5$ Hz, 2H, ArH), 4.47 (t, $J = 5.75$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{O}$), 4.27 (t, $J = 7.25$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.89 (t, $J = 5.75$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.56-3.43 (m, 24H, OCH_2), 3.35 (s, 9H, OCH_3), 1.90-1.85 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.42-1.25 (m, 14H, CH_2), 0.88 (t, $J = 7.0$ Hz, 3H, CH_2CH_3).

Figure S1. GPC trace of polymer **5**.

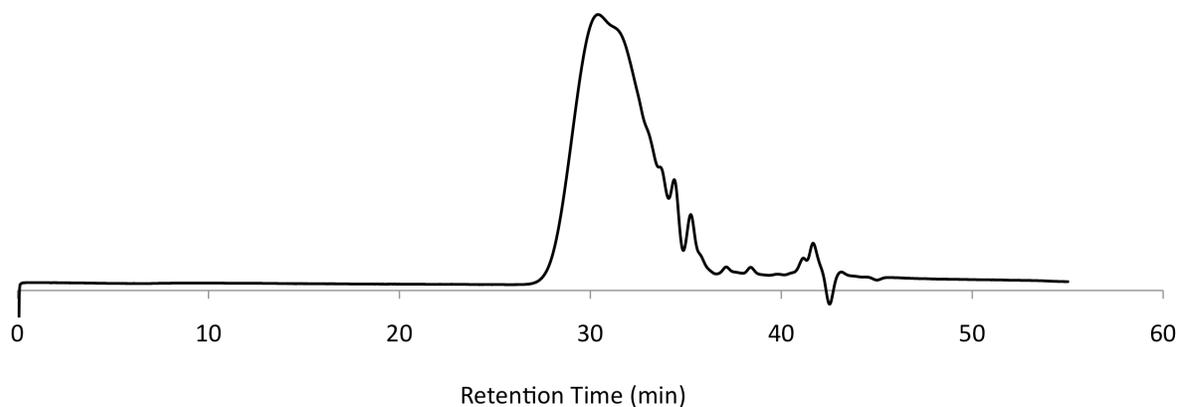


Figure S2. GPC trace of crude mixture of macrocycles **1b** and **6**.

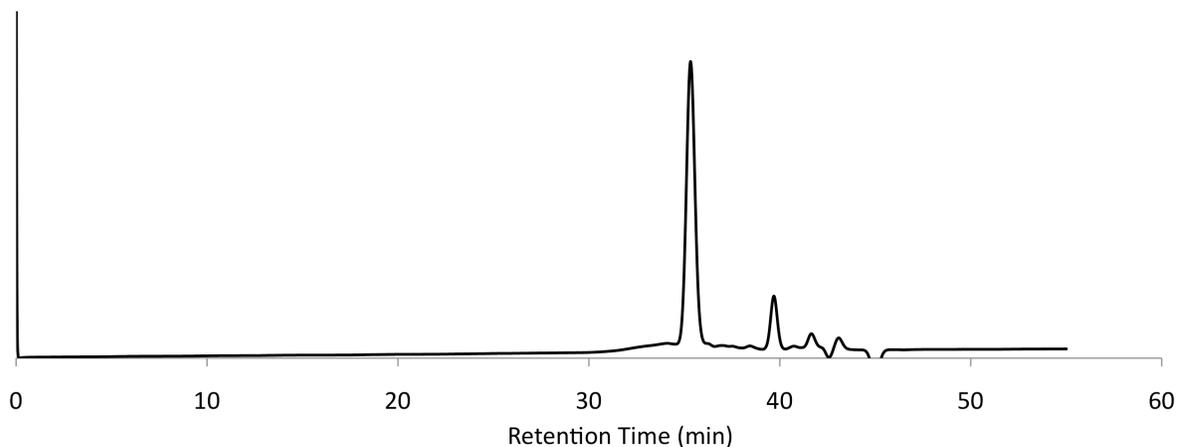


Figure S3. Overlaid GPC traces of macrocycles **6a** (blue, overlaps with **6b**), **6b** (red), **6c** and **6d** (green), **6e** (purple) and **1b** (orange).

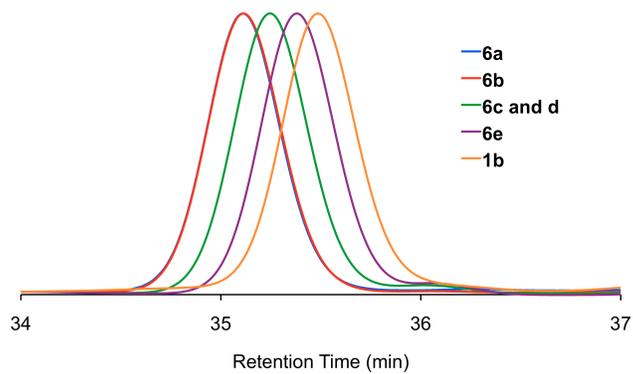
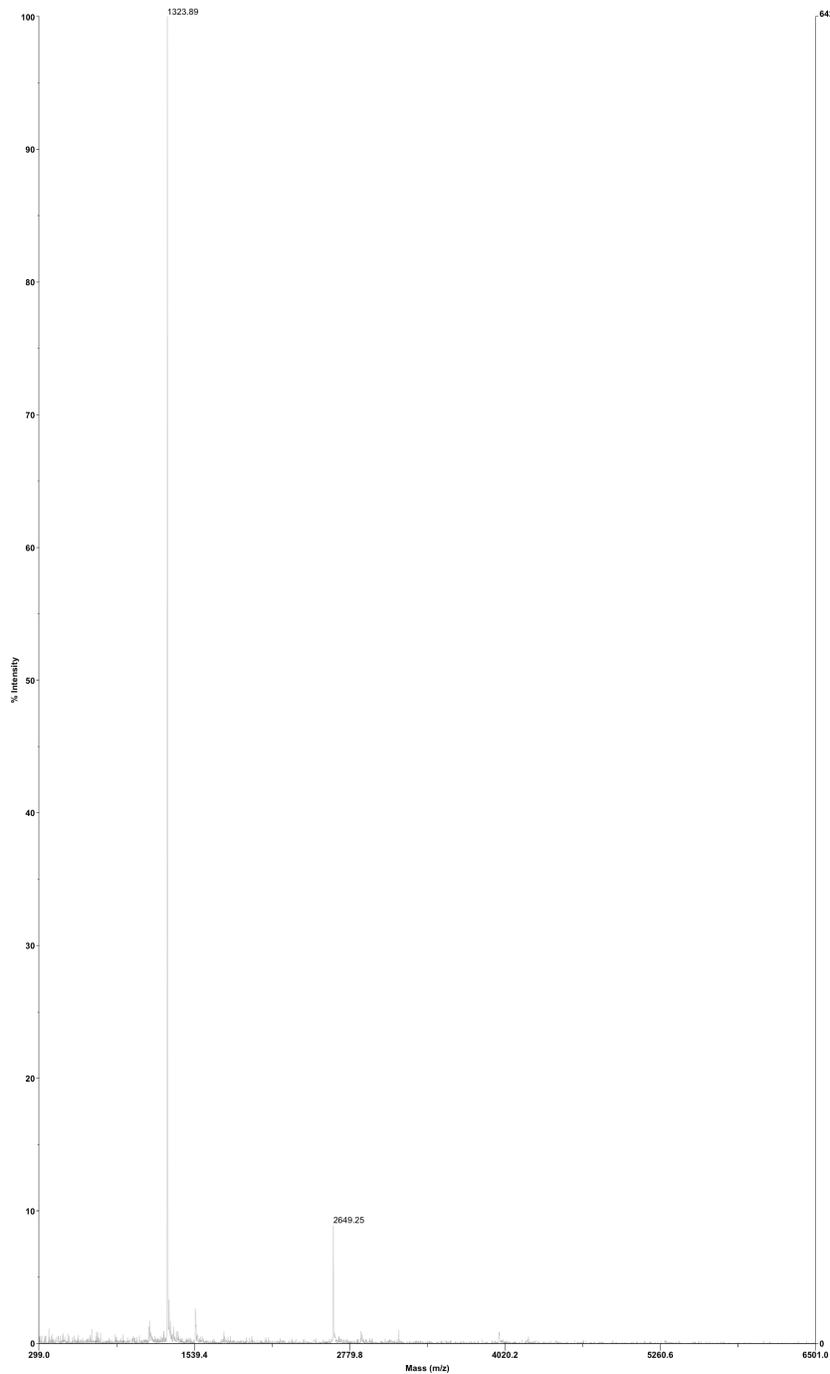


Figure S4. MALDI-MS of macrocycle **6b**.

Applied Biosystems Voyager System 4178

Voyager Spec #1[BP = 1323.6, 6427]



Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 92.5%
Guide wire 0: 0.05%
Extraction delay time: 130 nsec

Acquisition mass range: 300 -- 6500 Da
Number of laser shots: 200/spectrum
Laser intensity: 1780
Laser Rep Rate: 3.0 Hz
Calibration type: Default
Calibration matrix: Dithranol
Low mass gate: 100 Da

Digitizer start time: 17.258
Bin size: 1 nsec
Number of data points: 62558
Vertical scale: 500 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 37
Plate ID: 100 WELL PLATE
Serial number: 4178
Instrument name: Voyager-DE STR
Plate type filename: C:\VOYAGER\100 well plate.pl
Lab name: UIUC Mass Spec Lab

Absolute x-position: 32325
Absolute y-position: 32468.8
Relative x-position: 257.487
Relative y-position: 401.275
Shots in spectrum: 200
Source pressure: 1.775e-007
Mirror pressure: 2.592e-008
TC2 pressure: 0.001
TIS gate width: 30
TIS flight length: 1167

Acquired: 20:39:00, January 06, 2011

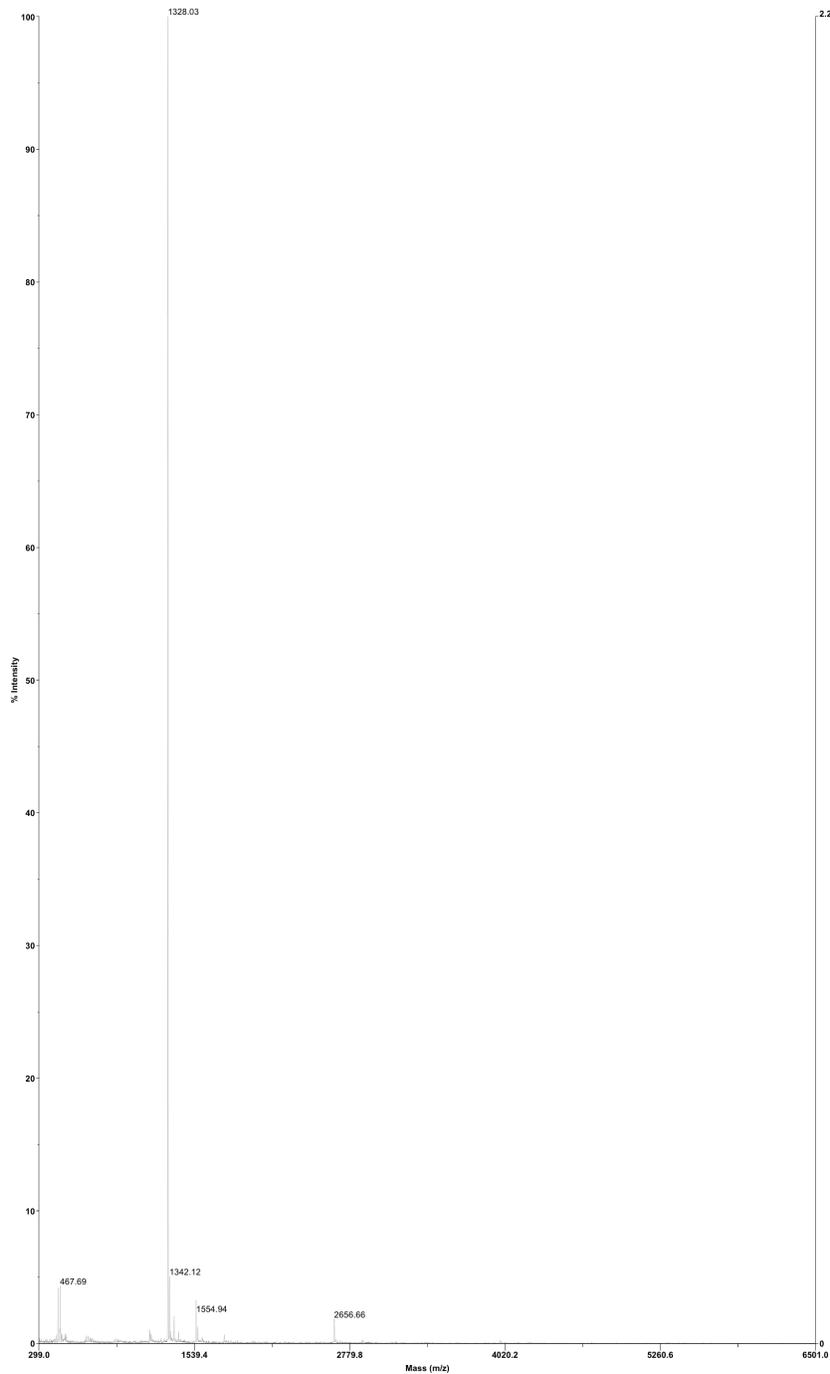
Printed: 19:58, January 06, 2011

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Figure S5. MALDI-MS of macrocycles **6c-d**.

Applied Biosystems Voyager System 4178

Voyager Spec #1[BP = 1328.1, 21796]



Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 92.5%
Guide wire 0: 0.05%
Extraction delay time: 130 nsec

Acquisition mass range: 300 -- 6500 Da
Number of laser shots: 200/spectrum
Laser intensity: 1740
Laser Rep Rate: 3.0 Hz
Calibration type: Default
Calibration matrix: Dithranol
Low mass gate: 100 Da

Digitizer start time: 17.258
Bin size: 1 nsec
Number of data points: 62558
Vertical scale: 500 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 27
Plate ID: 100 WELL PLATE
Serial number: 4178
Instrument name: Voyager-DE STR
Plate type filename: C:\VOYAGER\100 well plate.pl
Lab name: UIUC Mass Spec Lab

Absolute x-position: 31786.6
Absolute y-position: 37540.3
Relative x-position: -280.945
Relative y-position: 392.755
Shots in spectrum: 200
Source pressure: 1.441e-007
Mirror pressure: 2.388e-008
TC2 pressure: 0.001
TIS gate width: 30
TIS flight length: 1167

Acquired: 20:41:00, January 06, 2011

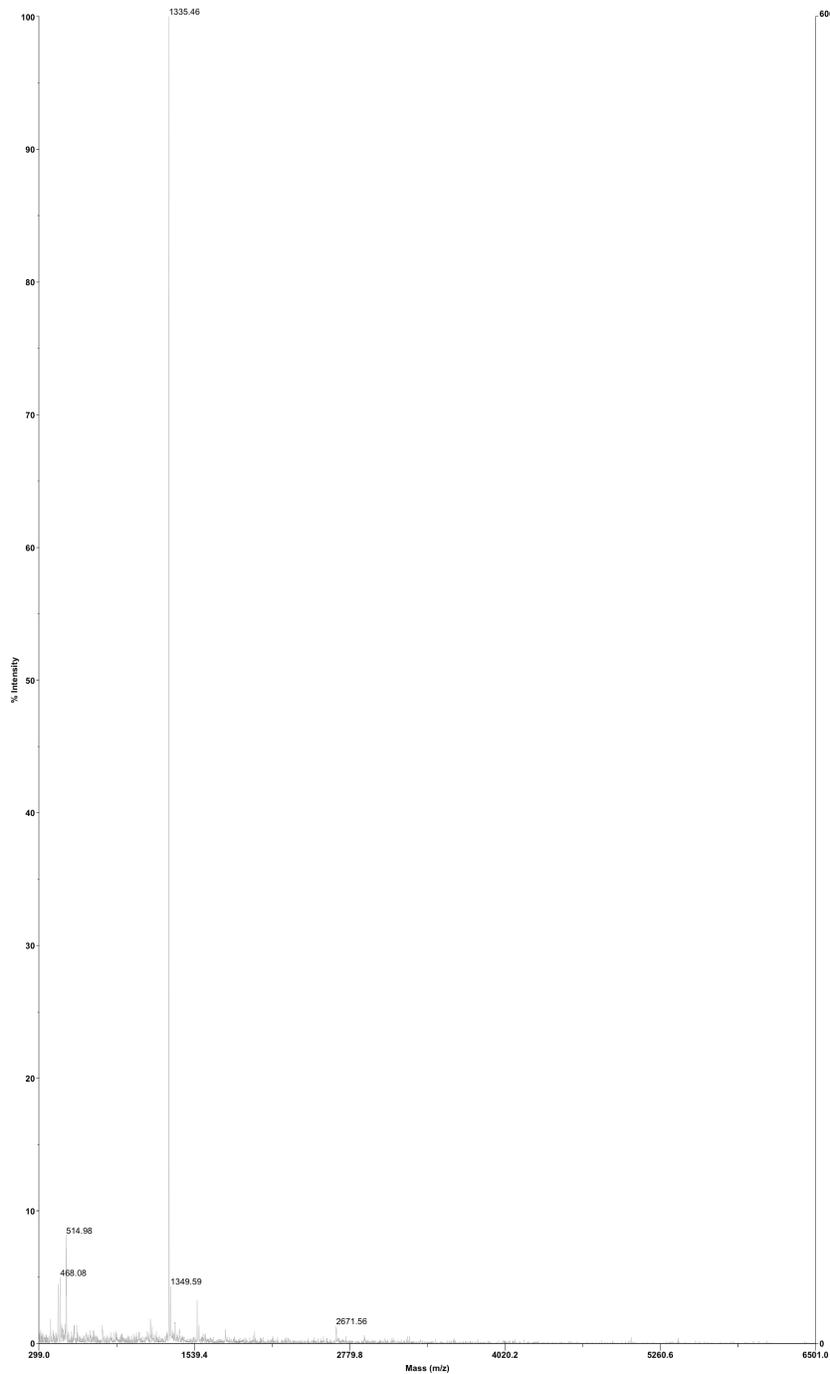
Printed: 19:57, January 06, 2011

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Figure S6. MALDI-MS of macrocycle **6e**.

Applied Biosystems Voyager System 4178

Voyager Spec #1[BP = 1335.4, 6065]



Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 92.5%
Guide wire 0: 0.05%
Extraction delay time: 130 nsec

Acquisition mass range: 300 -- 6500 Da
Number of laser shots: 200/spectrum
Laser intensity: 1740
Laser Rep Rate: 3.0 Hz
Calibration type: Default
Calibration matrix: Dithranol
Low mass gate: 100 Da

Digitizer start time: 17.258
Bin size: 1 nsec
Number of data points: 62558
Vertical scale: 500 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 17
Plate ID: 100 WELL PLATE
Serial number: 4178
Instrument name: Voyager-DE STR
Plate type filename: C:\VOYAGER\100 well plate.pl
Lab name: UIUC Mass Spec Lab

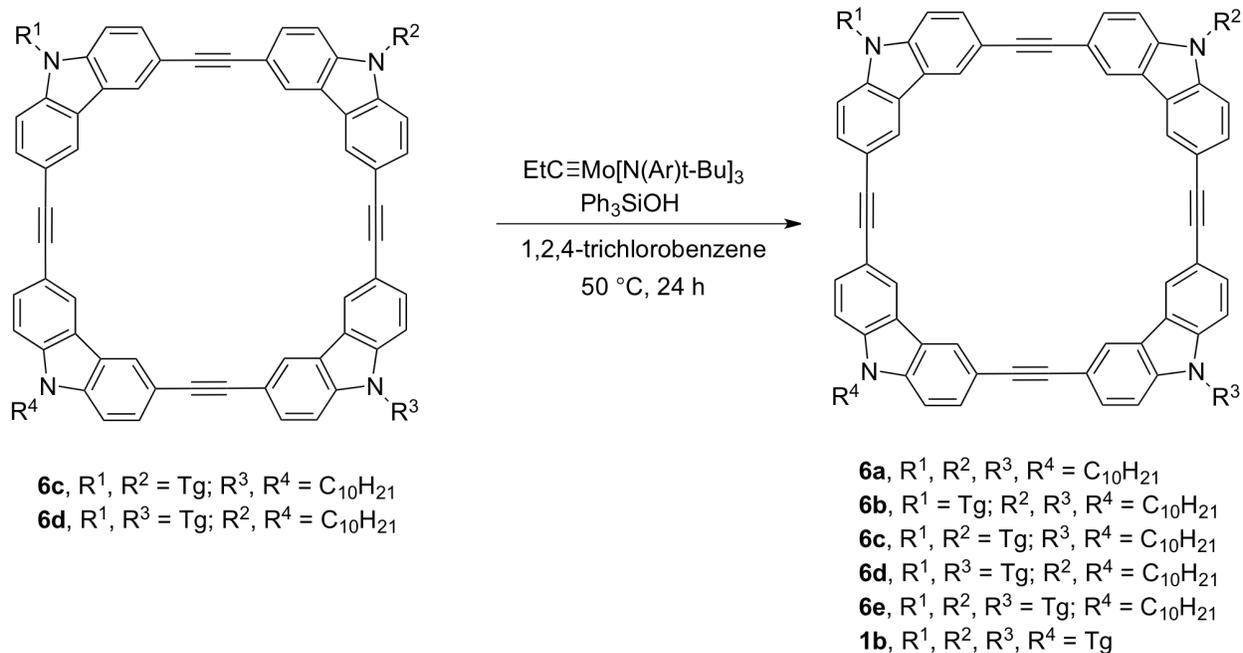
Absolute x-position: 32860.6
Absolute y-position: 42076.4
Relative x-position: 793.066
Relative y-position: -151.107
Shots in spectrum: 200
Source pressure: 1.257e-007
Mirror pressure: 2.239e-008
TC2 pressure: 0.001
TIS gate width: 30
TIS flight length: 1167

Acquired: 20:43:00, January 06, 2011

Printed: 19:59, January 06, 2011

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Figure S7. Dynamic experiment 1: Ring opening and scrambling of carbazole tetracycles and crude MALDI spectrum.



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Comment 1 Gross, Dustin
Comment 2 DHB

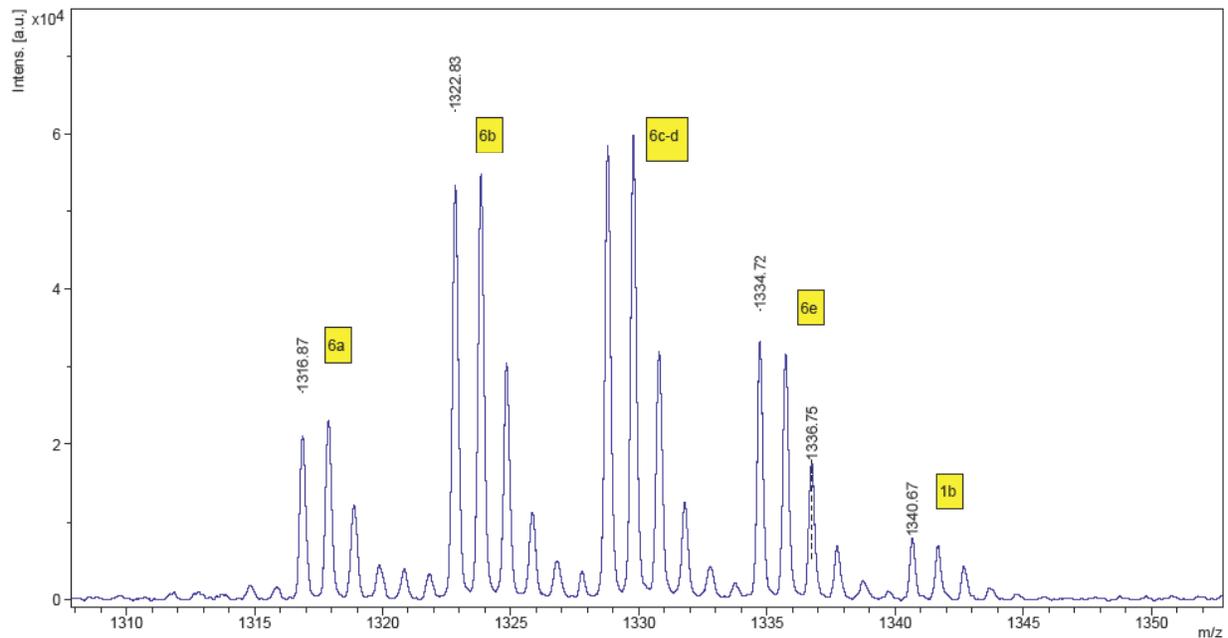
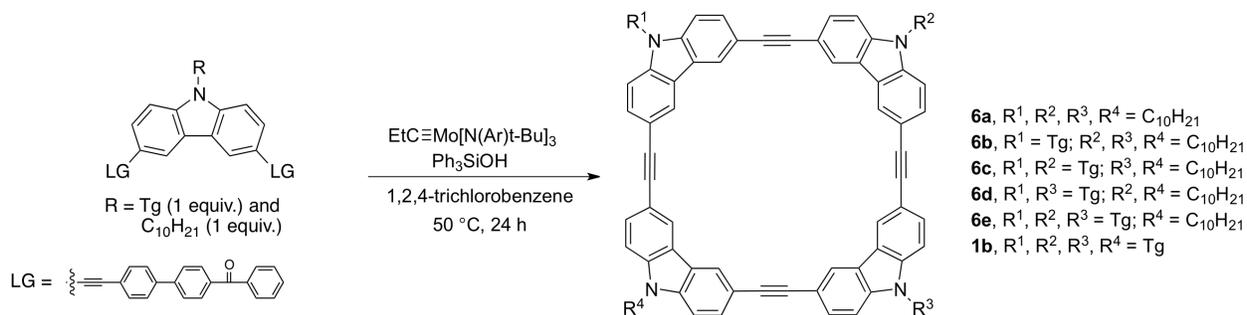
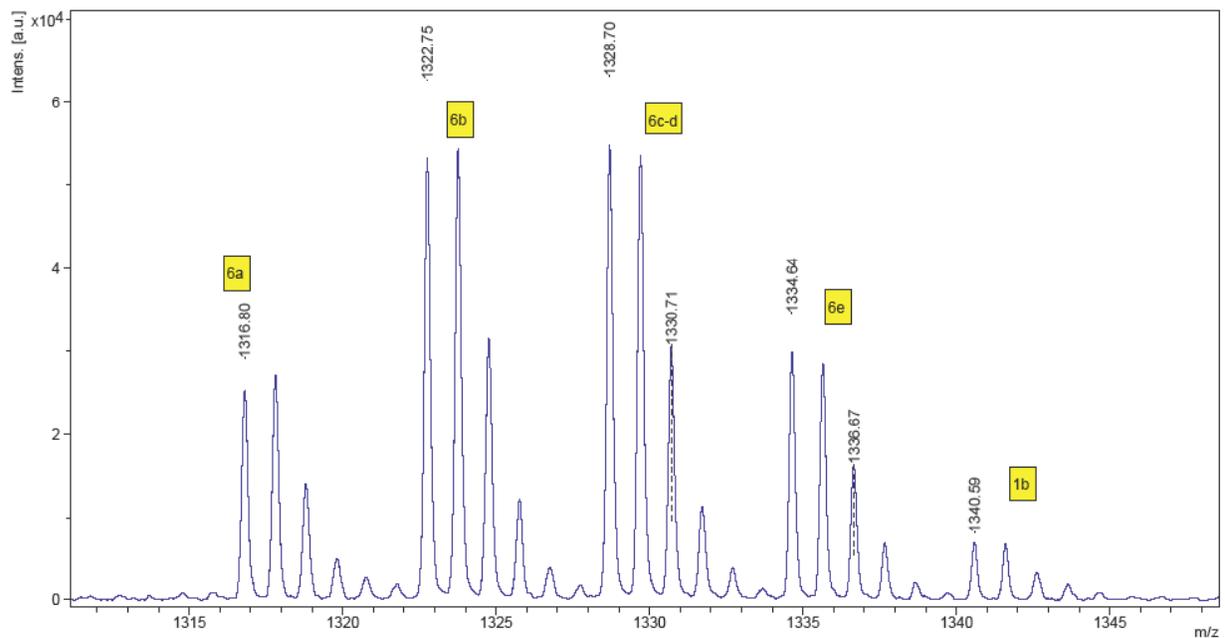


Figure S8. Dynamic experiment 2: Metathesis of benzoylbiphenyl substituted monomers and crude MALDI spectrum.



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Comment 1 Gross, Dustin
Comment 2 DHB



Synthesis of Carbazolyl-(*p*-phenylene)-ethynylene Copolymers and Macrocycles

Polymer 8. In an argon filled glovebox, an oven dried vial was loaded with 9-((2-(2-ethoxyethoxy)ethoxy)methyl)-3,6-diethynyl-9-carbazole² **3** (377 mg, 1.0 mmol), 1,4-bis(2-ethylhexyl)-2,5-diiodobenzene **7** (554 mg, 1 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol, 0.042 equiv.), CuI (4 mg, 0.021 mmol, 0.016 equiv), and dissolved in piperidine (9 mL). The mixture was sealed, removed from the glove box and heated at 50 °C for 72 hours. The reaction was then cooled to room temperature and poured into a flask containing MeOH (200 mL) to precipitate the co-polymer. The solid was collected by filtration and dried in vacuo to yield 780 mg of polymer **8**. GPC (THF): M_n = 9500 g/mol, M_w = 22000 g/mol, PDI = 2.5, ret. time = 25.2 min.)

Macrocycle 9 from polymer 8. In an argon filled glovebox, an oven dried vial was loaded with molybdenum catalyst³ (10 mg, 0.015 mmol, 10 wt%), Ph₃SiOH (20 mg, 0.072 mmol, 20 wt%), and dissolved in 1,2,4-trichlorobenzene (8 mL). The orange-brown solution was stirred for 5 minutes then polymer **8** (100 mg) dissolved in 1,2,4-trichlorobenzene (8 mL) was added. The vial was sealed, removed from the glovebox, and left to stir at room temperature for 24 hrs. The 1,2,4-trichlorobenzene was removed by vacuum distillation and the product was purified by silica gel column chromatography eluting with Ethyl Acetate:Hexanes (1:1), yielding macrocycle **9** (41 mg, 41%) as a white solid. GPC of the crude reaction mixture, (THF): M_n = 3300 g/mol, M_w = 6100 g/mol, PDI = 1.8, ret. time = 28.7 min.). GPC of macrocycle **9**, (THF): M_n = 2800 g/mol, M_w = 2850 g/mol, PDI = 1.0, ret. time = 28.9 min.). ¹H NMR (CDCl₃, 500 MHz): δ 8.30 (s, 8H), 7.67 (d, *J* = 8.5 Hz, 8H), 7.47 (d, *J* = 8.5 Hz, 8H), 7.42 (s, 8H), 4.53 (t, 8H), 3.91 (t, *J* = 5 Hz, 8H), 3.56-3.43 (m, 32H), 3.35 (s, 12H), 2.86 (m, 16H), 1.91 (m, 8H), 1.45-1.25 (m, 64H), 0.99 (t, 24H), 0.93 (t, 24H); ¹³C NMR (CDCl₃, 125 MHz): δ 140.9, 140.6, 133.4, 129.5, 123.9, 122.8, 122.6, 114.5, 109.4, 94.9, 87.6, 71.8, 71.0, 70.6, 70.6, 69.4, 59.0, 40.4, 38.7, 32.6, 29.0, 25.6, 23.2, 14.2, 10.9 MALDI-TOF *m/z* = 2638.

Figure S9. GPC traces for polymer **8** and macrocycle **9**.

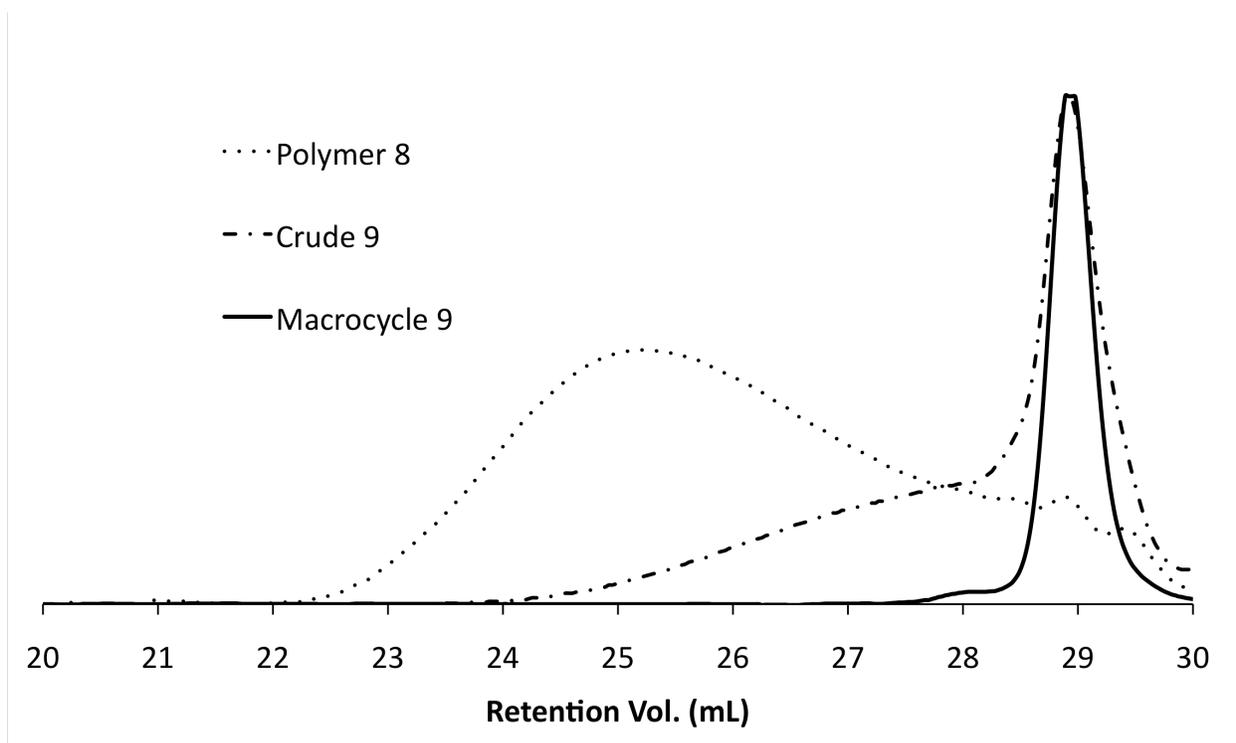


Figure S10. ^1H NMR for macrocycle **9**.

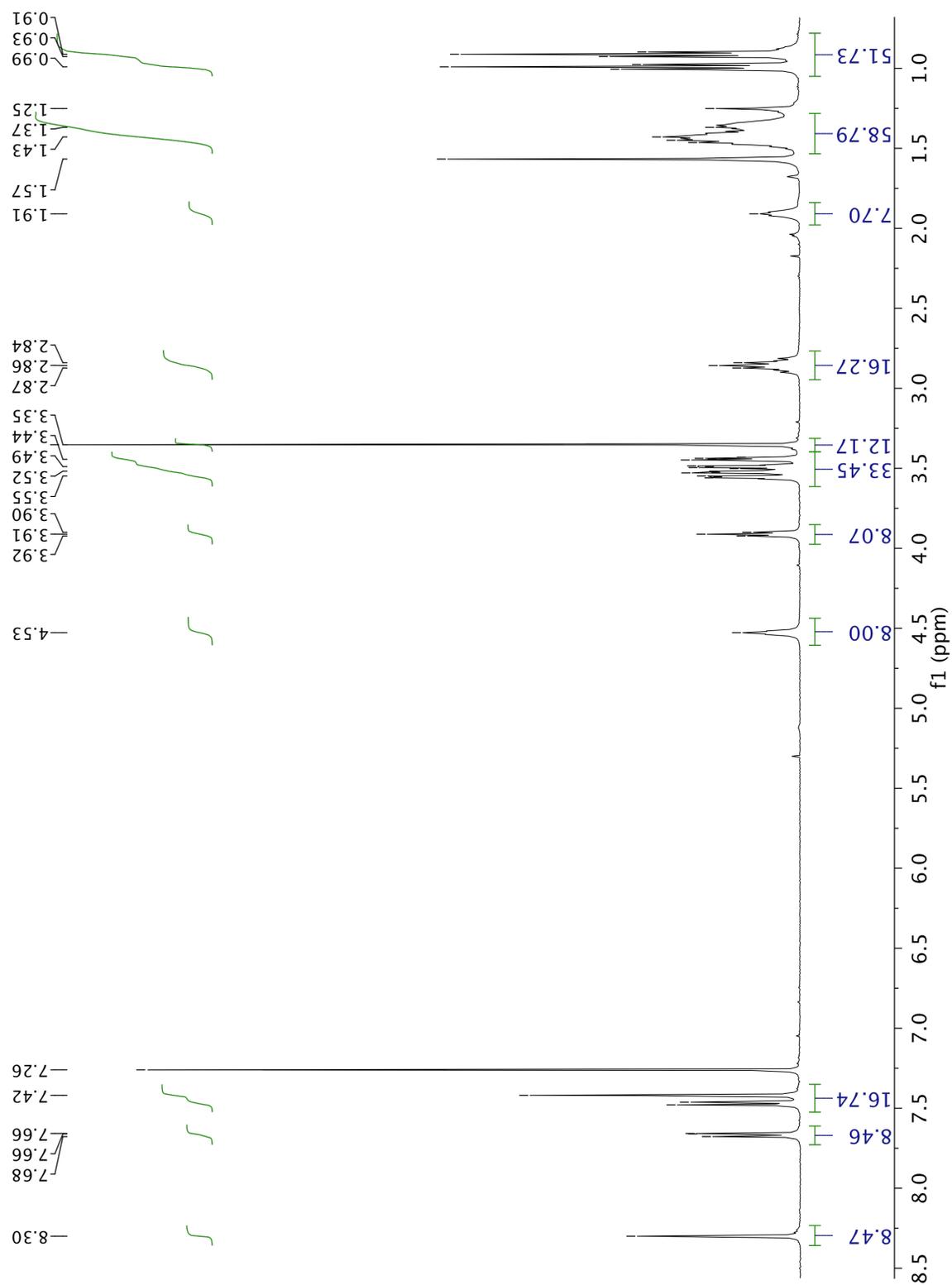


Figure S11. ^{13}C NMR for macrocycle **9**.

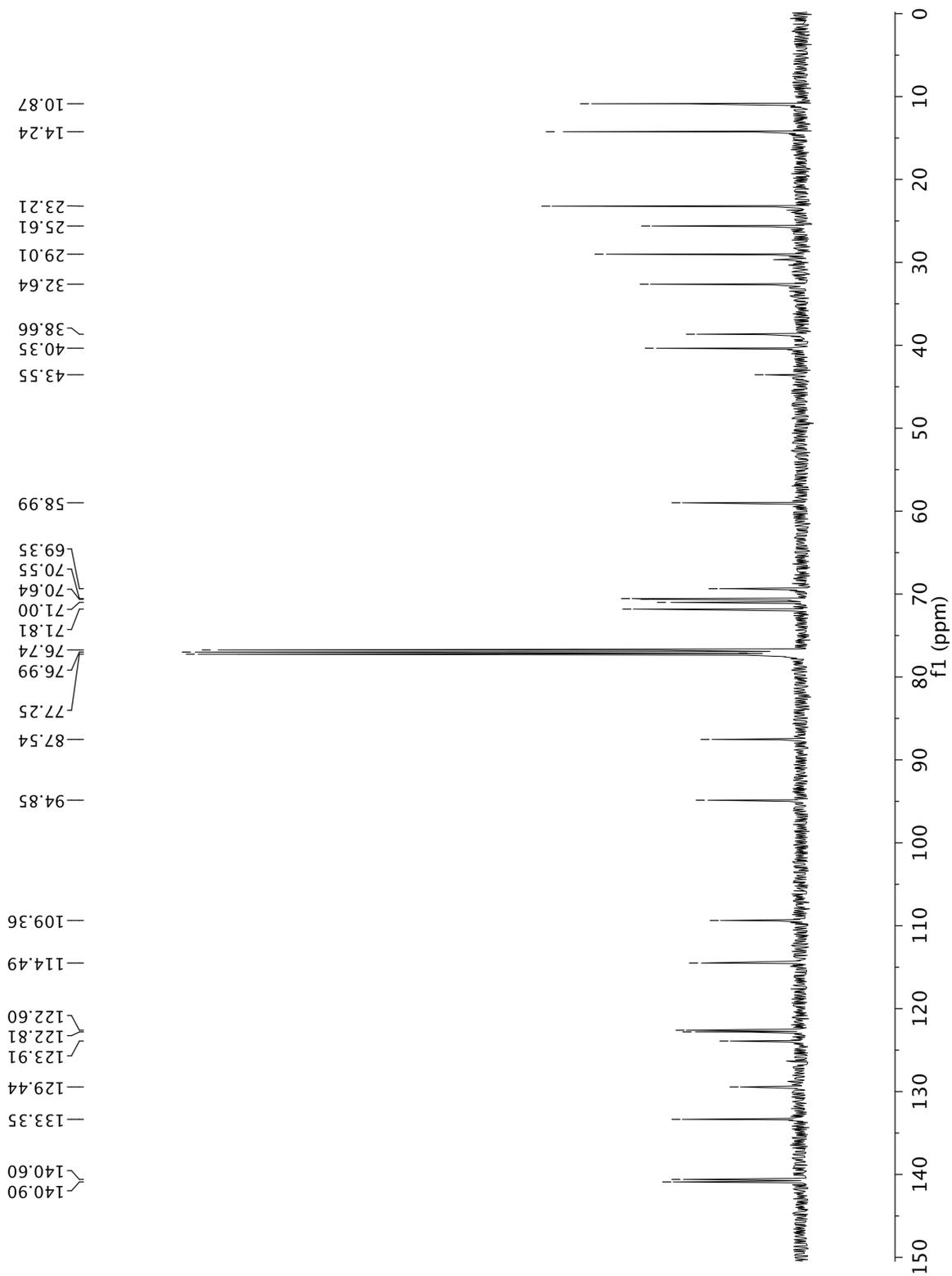


Figure S12. MALDI-MS for the crude products when polymer **8** was subjected to metathesis.

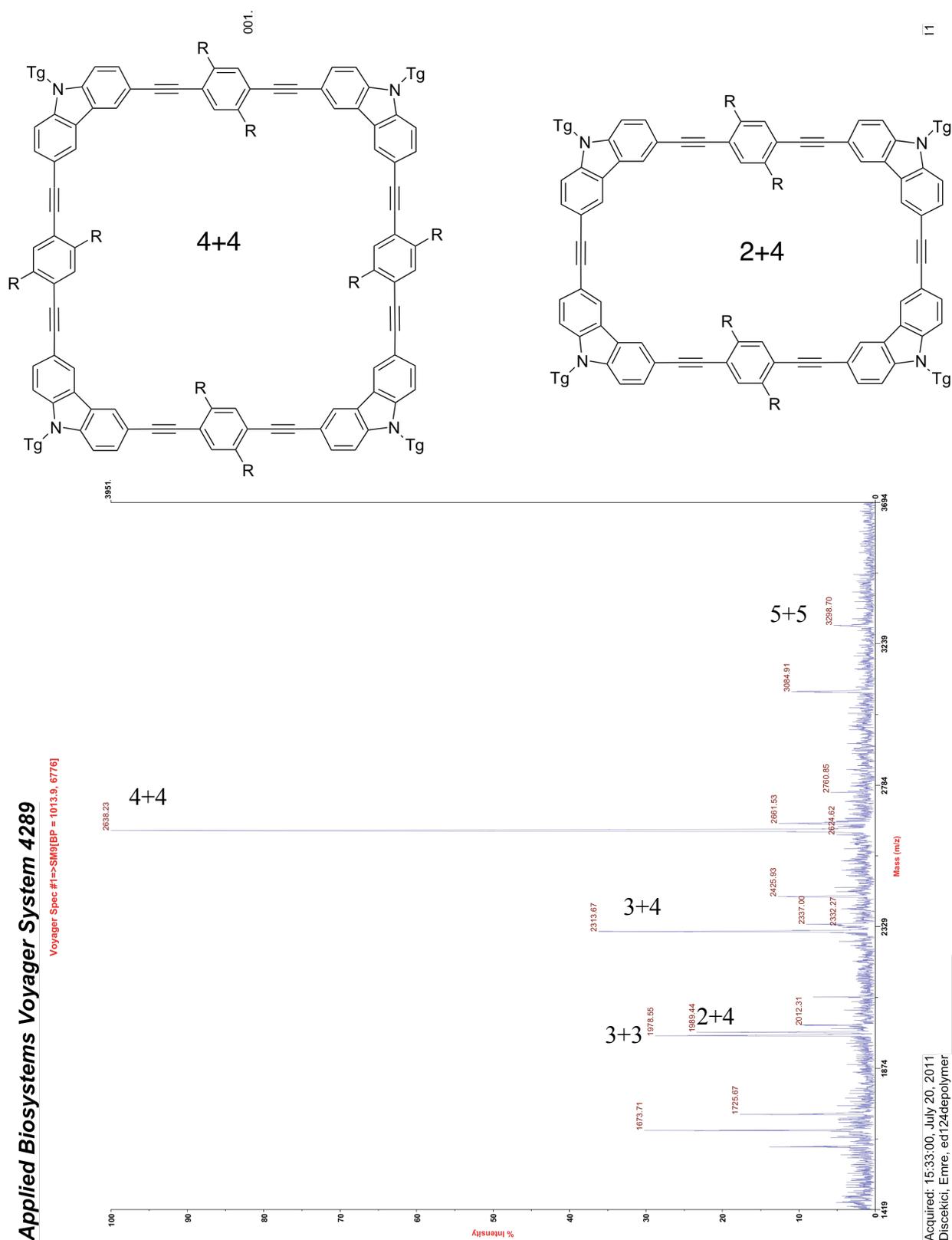
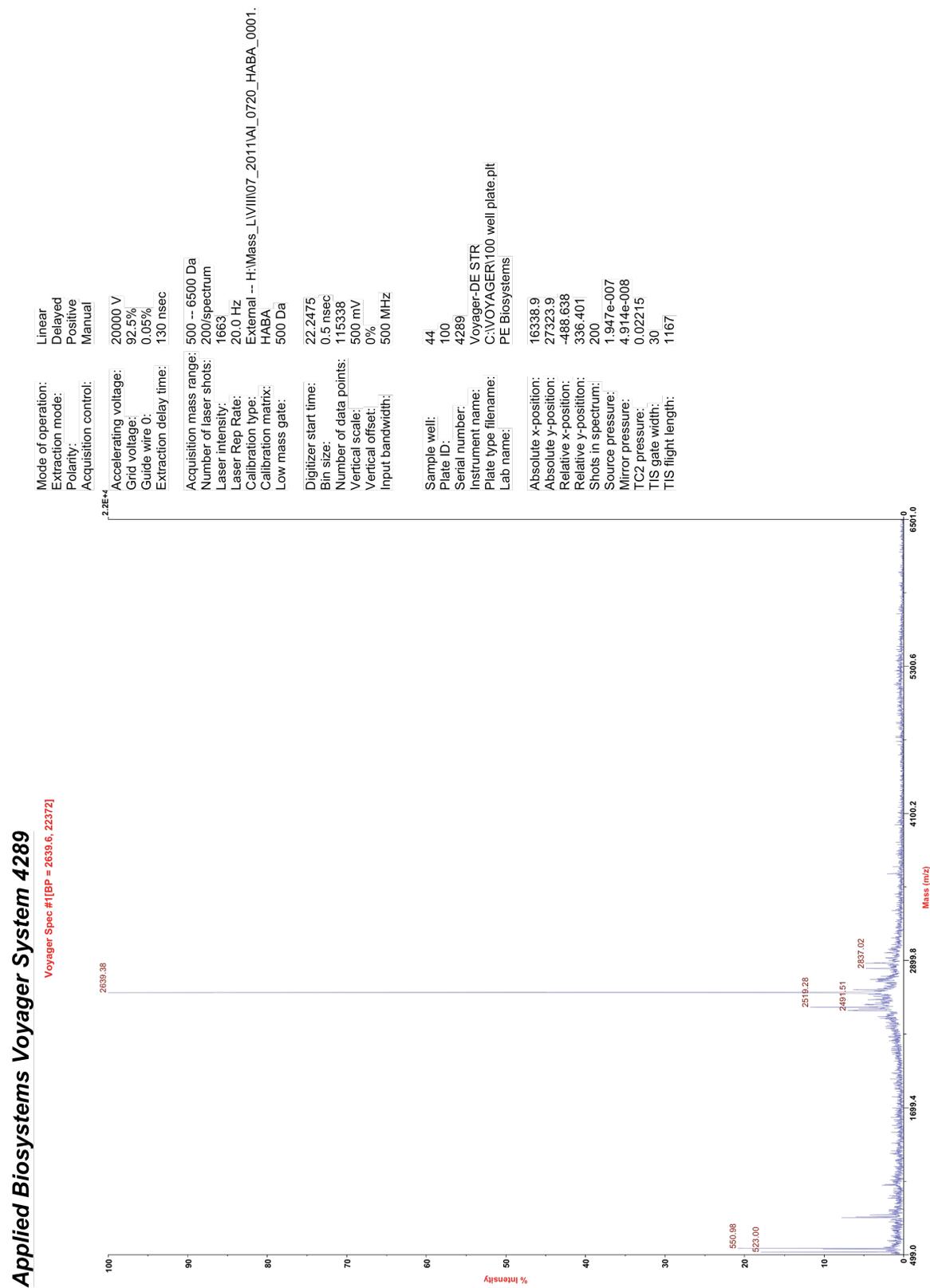


Figure S13. MALDI-MS for macrocycle **9**.



Synthesis of Carbazolyl-(*m*-phenylene)-ethynylene Copolymers and Macrocycles

Polymer 11 from 3 and 10. In an argon filled glovebox an oven dried vial was loaded with 1,5-bis(hexyloxy)-2,4-diiodobenzene **10** (1.54 g, 2.9 mmol, 1 equiv.), **3**² (1.05 g, 2.9 mmol, 1 equiv.), Pd(PPh₃)₄ (168 mg, 0.15 mmol, 0.05 equiv.), CuI (28 mg, 0.15 mmol, 0.05 equiv.), dry THF (10 mL) and piperidine (5 mL). The vial was sealed, removed from the box and heated at 60 °C for 48 hrs. The reaction was then cooled and poured into a flask containing MeOH (400 mL) to precipitate the polymer. The solid was collected by filtration and dried under vacuum to yield 1.54 g of polymer **11**. GPC (THF): Mn = 5100 g/mol, Mw = 9700 g/mol, PDI = 1.9, ret. time = 31.5 min.)

Macrocycles from the Depolymerization of 11. In an argon filled glovebox an oven dried vial was loaded with molybdenum catalyst³ (10 mg, 0.015 mmol, 10 wt%), Ph₃SiOH (20 mg, 0.072 mmol, 20 wt%), and 1,2,4-trichlorobenzene (5 mL). The orange-brown solution was stirred for 5 minutes then polymer **11** (100 mg) was added. The vial was sealed, removed from the box and heated at 50 °C for 24 hrs. Multiple products (>5) were observed by TLC in DCM:Hexanes (2:1). The 1,2,4-trichlorobenzene was removed by vacuum distillation. GPC for the crude reaction mixture showed two peaks (see below) (THF): Mn = 2100 g/mol, PDI = 1.37, ret. time = 35.0 and 35.6 min.)

Figure S14. GPC traces for polymer **11** and the crude depolymerization.

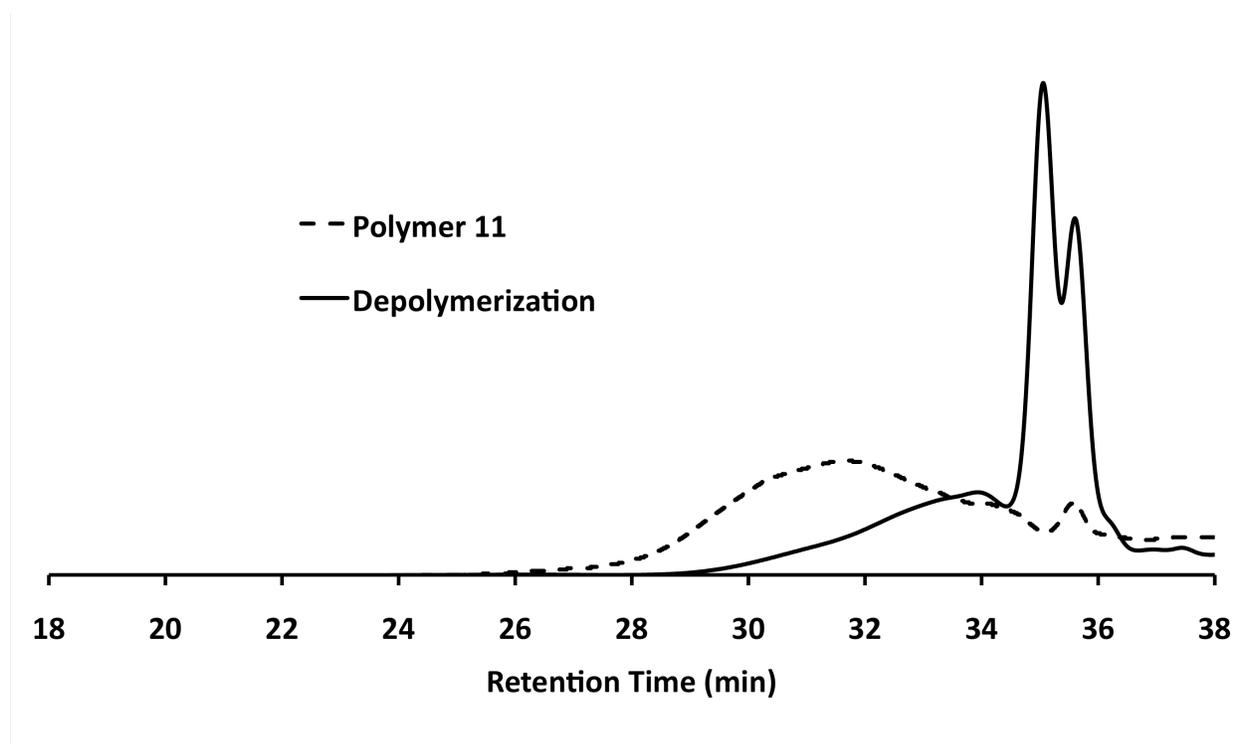
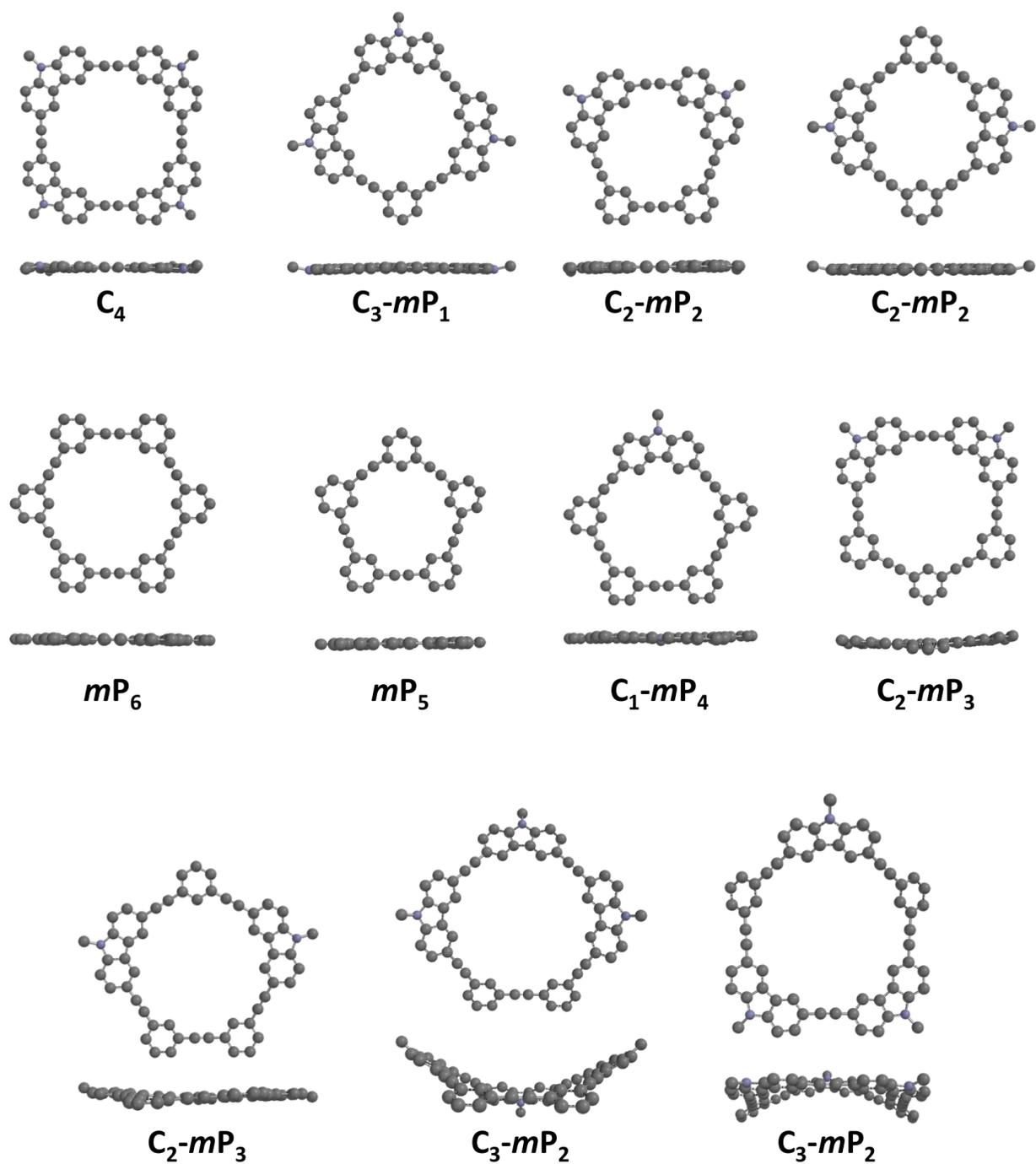


Figure S15. AM1 optimized structures of carbazolyl-*m*phenylene ethynylene hybrid macrocycles



References

- ¹ A. D. Finke, D. E. Gross, A. Han, and J. S. Moore, *J. Am. Chem. Soc.*, 2011, **133**, 14063.
- ² D. E. Gross and J. S. Moore, *Macromolecules*, 2011, **44**, 3685.
- ³ W. Zhang, S. Kraft, and J. S. Moore, *Chem. Commun.*, 2003, 832.