Supporting Information for:

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

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General Page S2

Synthesis and characterization of:

   Carbazolyl-ethynylene systems Page S3
   Carbazolyl-(p-phenylene)-ethynylene systems Page S11
   Carbazolyl-(m-phenylene)-ethynylene systems Page S17
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 Thermoseparations 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 (705 mg, 1.26 mmol, 1 equiv.), 3 (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 vaccuo 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.

**Macrocycles (1b and 6) from Polymer (5).** In an argon filled glovebox an oven dried vial was loaded with molybdenum catalyst (40 mg, 0.06 mmol, 6.3 wt%), Ph$_3$SiOH (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, 53%), 6e (89 mg, 15%), and 1b (38 mg, 60%). 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.

6a $^1$H 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).

6b $^1$H 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, NCH₂CH₂CH₂), 3.92 (t, J = 5.75 Hz, 2H, NCH₂CH₂O), 3.57-3.43 (m, 8H, OCH₂), 3.36 (s, 3H, OCH₃), 1.92-1.89 (m, 6H, NCH₂CH₂CH₂), 1.42-1.26 (m, 42H, CH₂), 0.88 (t, J = 7.0 Hz, 9H, CH₂CH₃).

6c-d ¹H NMR (500 MHz, CDCl₃): 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, NCH₂CH₂O), 4.30 (t, J = 7.25 Hz, 4H, NCH₂CH₂CH₂), 3.91 (t, J = 5.75 Hz, 4H, NCH₂CH₂O), 3.57-3.43 (m, 16H, CH₂), 3.35 (s, 6H, OCH₃), 1.91-1.88 (m, 4H, NCH₂CH₂CH₂), 1.42-1.22 (m, 28H, CH₂), 0.88 (t, J = 7.0 Hz, 6H, CH₂CH₃).

6d ¹H NMR (500 MHz, CDCl₃): 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, NCH₂CH₂O), 4.27 (t, J = 7.25 Hz, 2H, NCH₂CH₂CH₂), 3.89 (t, J = 5.75 Hz, 6H, NCH₂CH₂O), 3.56-3.43 (m, 24H, OCH₂), 3.35 (s, 9H, OCH₃), 1.90-1.85 (m, 2H, NCH₂CH₂CH₂), 1.42-1.25 (m, 14H, CH₂), 0.88 (t, J = 7.0 Hz, 3H, CH₂CH₃).

Figure S1. GPC trace of polymer 5.

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

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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**

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

**Applied Biosystems Voyager System 4178**

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

**Applied Biosystems Voyager System 4178**

Voyager SpecD (SP # 11204.6, 6665)

- **Mode of operation:** Linear
- **Extraction mode:** Delayed
- **Polarity:** Positive
- **Acquisition control:** Manual
- **Accelerating voltage:** 20000 V
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- **Guide wire 0:** 0.05%
- **Extraction delay time:** 130 nsec
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**Lab name:** UIC Mass Spec Lab

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

6c, R¹, R² = Tg; R³, R⁴ = C¹₀H₂₁
6d, R¹, R³ = Tg; R², R⁴ = C¹₀H₂₁
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
Figure S8. Dynamic experiment 2: Metathesis of benzoylbiphenyl substituted monomers and crude MALDI spectrum.
**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-carbazole<sup>2</sup> 3 (377 mg, 1.0 mmol), 1,4-bis(2-ethylhexyl)-2,5-diodobenzene 7 (554 mg, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (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 vacuum to yield 780 mg of polymer 8. GPC (THF): M<sub>n</sub> = 9500 g/mol, M<sub>w</sub> = 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 catalyst<sup>3</sup> (10 mg, 0.015 mmol, 10 wt%), Ph<sub>3</sub>SiOH (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): Mn = 3300 g/mol, M<sub>w</sub> = 6100 g/mol, PDI = 1.8, ret. time = 28.7 min.). GPC of macrocycle 9, (THF): Mn = 2800 g/mol, M<sub>w</sub> = 2850 g/mol, PDI = 1.0, ret. time = 28.9 min.). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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 = 8.5 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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. $^1$H 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.), 32 (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