Supporting Information

Cooperative Self-Assembly of Oligo(m-phenyleneethynylenes) into Supramolecular Coordination Polymers

Jay Wm. Wackerly and Jeffrey S. Moore*

Departments of Chemistry and Materials Science and Engineering, Roger Adams Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
moore@scs.uiuc.edu

Figure 1S. $^1$H NMR of oligomer 2 with 0 equiv (bottom), 0.5 equiv, 1 equiv, and 3 equiv PdCl$_2$(CH$_3$CN)$_2$ (top) in chloroform-d at 0.19 mM.
Figure 2S. Raw ITC injection data for the titration of a 0.10 mM solution of 1 with a 1.33 mM solution of $trans$-dichlorobis(acetonitrile)palladium in acetonitrile at 20 °C.

Figure 3S. Raw ITC injection data for the titration of a 0.10 mM solution of 2 with a 1.33 mM solution of $trans$-dichlorobis(acetonitrile)palladium in acetonitrile at 20 °C.
**Figure 4S.** Raw ITC injection data for the titration of a 0.10 mM solution of 3 with a 1.33 mM solution of *trans*-dichlorobis(acetonitrile)palladium in acetonitrile at 20 °C.

**Figure 5S.** Raw ITC injection data for the titration of a 0.10 mM solution of 12 with a 1.33 mM solution of *trans*-dichlorobis(acetonitrile)palladium in acetonitrile at 20 °C.
**Experimental Procedures**

**General.** Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. All air- or moisture-sensitive reactions were performed under an atmosphere of dry argon or nitrogen. Analytical thin-layer chromatography was performed with Kieselgel F-254 pre-coated TLC plates. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from EM Science or Silicycle. Triethylamine was distilled under argon and collected over 3 Å molecular sieves. The $^1$H and $^{13}$C NMR spectra were recorded on a Varian Unity 500 or Varian Utility Inova 500 MHz Narrow Bore spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent peaks as internal standard for chloroform-d (δ 7.26 ppm for $^1$H and δ 77.0 ppm for $^{13}$C), DMSO-d$_6$ (δ 2.50 ppm for $^1$H and 39.51 ppm for $^{13}$C), and acetonitrile-d$_3$ (δ 1.94 ppm for $^1$H). Coupling constants, $J$, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Electron ionization (EI) and matrix-assisted laser desorption (MALDI) mass spectra were obtained through the Mass Spectrometry Facility, School of Chemical Sciences, University of Illinois at Urbana-Champaign. Elemental analyses were performed by the University of Illinois Micro Analytical Service Laboratory.

Analytical gel permeation chromatography was performed with a Waters 515 HPLC pump, a Spectraseries AS100 autosampler, a Viscotek model 300 triple detector array, and a series of three Vistotek (7.8 x 300 mm) Viscogel columns (2x GMHHRH and 1x G3000H). Data were obtained in a solution of 89% tetrahydrofuran, 10% ethanol, and 1% triethylamine at 30 °C. Purity was determined by integration of the peak corresponding to the macromolecule versus the integration of the entire run using the refractive index detector at a flow rate of 1.0 mL/min.
All UV absorbance data were recorded with a Shimadzu (model UV-2501) spectrophotometer using a 1.0 cm path length quartz cell at a thermostated temperature of 25 °C. All measurements were recorded using spectroscopic grade acetonitrile purchased from Fisher Scientific.

Isothermal microcalorimetry data collected with a MCS Isothermal Titration Calorimetry System. All measurements were recorded using spectroscopic grade acetonitrile purchased from Fisher Scientific at an isothermal temperature of 20 °C. In a typical titration a 0.10 mM solution of the oligomer was placed in the sample cell until a constant temperature of 20 °C was reached. Then the titrant consisting of trans-dichlorobis(acetonitrile)palladium in acetonitrile at a concentration of 1.33 mM was loaded into the 250 µL automatic titration syringe. An initial injection of 4 µL was performed and the remaining titrant was added in 24 injections of 10 µL each spaced 1500 seconds apart for the first three injections then ramped down by 50 seconds per injection until 750 seconds where it remained for the final seven injections. Heat of dilution was corrected by adding trans-dichlorobis(acetonitrile)palladium tritrant to acetonitrile without oligomer. The enthalpy of binding and association constant for the binding and folding (or stacking) of the oligomers with palladium were determined with the curve fitting program Origin form MicroCal inc. The stoichiometry of one oligomer to one palladium was inputted into the model. All experiments were performed in duplicate.

Nomenclature of Oligomers. All oligomers dimer length and longer are designated using an abbreviated nomenclature system. The naming scheme follows the pattern: X-[A]n-X. The end group X can indicate a 3-Ethynyl-5-{2-[2-(2-methoxyethoxy) ethoxy] ethoxymethyl} pyridine (Pyr), a bromide (Br), trimethylsilylethylene (−≡−TMS), or an ethynylene group (−≡−H). The substituent A corresponds to the m-phenyleneethynylene unit with a triethylene glycol mono
methyl ether chain \( m \) to the oligomer backbone. The \( n \) represents the number of repeating \( m \)-phenyleneethynylene units.

**Synthesis.**

![N-O-Br](image)

**3-Bromo-5-hydroxymethyl-pyridine (4).** The synthesis of 4 has been previously reported\(^1\) however a higher yielding procedure with thorough characterization is described here. A solution of 3-bromonicotinic acid (10.378 g, 51.373 mmol) in distilled THF (200 mL) was cooled in an ice bath at 0 °C. A borane-THF complex in THF (1 M, 100 mL) was slowly added and after the addition was complete the mixture was warmed to r.t. After 24 h the solution was cooled back down in an ice bath at 0 °C and quenched by the slow addition of NaOH solution (3 M, 40 mL), then NaOH pellets were added until the pH > 11. After 12 h of stirring sodium bicarbonate was added to the solution (200 mL). The organic and aqueous layers were separated and the aqueous phase was extracted with THF (3 × 200 mL). The combined organic layers were washed with H\(_2\)O (300 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed *in vacuo* to give a yellow oil. Purification by silica gel flash chromatography (ethyl acetate) gave 2.885 g (15.26 mmol, 30%) of 4 as an orange oil: \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \( \delta \) 8.58 (d, J=2.4 Hz, 1H, 4), 8.51 (d, J=1.8 Hz, 1H, 3), 7.96 (dd, J=2.3, 1.8 Hz, 1H, 1), 5.46 (t, J=5.8 Hz, 1H, 7), 4.54 (dd, J=5.8, 0.5 Hz, 2H, 6); \(^1^3\)C NMR (126 MHz, DMSO-d\(_6\)) \( \delta \) 148.6 (4), 146.6 (3), 140.2 (5), 136.7 (1), 120.1 (2), 59.9 (6); EI MS (m/v) calcd for C\(_6\)H\(_6\)NOBr 186.9633, found 186.9631; TLC \( R_f = 0.30 \) (ethyl acetate); Anal. Calcd for C\(_6\)H\(_6\)N\(_1\)O\(_1\)Br\(_1\) C 38.33, H 3.22, N 7.45, found C 38.63, H 3.23, N 7.27.
3-Bromo-5-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxymethyl}-pyridine (5). To a solution of KOH (1.660 g, 29.58 mmol) in DMSO (10 mL) 4 (2.741 g, 14.58 mmol) was added and heated in an oil bath at 60 °C. After 1 h 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl p-tosylate\textsuperscript{2} (5.618 g, 17.65 mmol) was added to the solution and heated to 70 °C for 3 h. The reaction mixture was diluted with ether and aqueous NH\textsubscript{4}Cl. The layers were separated and the aqueous phase was extracted with ether (4 × 100 mL). The combined organic layers were washed with H\textsubscript{2}O (200 mL) and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed \textit{in vacuo} to give a brown oil. Purification by silica gel flash chromatography (ethyl acetate) gave 3.595 g (10.76 mmol, 74%) of 5 as a yellow oil: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.55 (d, \(J = 2.2\) Hz, 1H, 4), 8.44 (d, \(J = 1.8\), 1H, 3), 7.84 (dd, \(J = 2.2, 1.8\) Hz, 1H, 1), 4.54 (d, \(J = 0.5\), 2H, 6), 3.67-3.61 (m, 10H, 7-11), 3.51 (m, 2H, 12), 3.34 (s, 3H, 13); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 149.9 (4), 146.9 (3), 137.7 (1), 135.6 (5), 120.7 (2), 71.8 (12), 70.6-70.4 (4 peaks, 6,8-10), 70.0 (11) 69.7 (7), 58.9 (13); EI MS (\(m/\nu\)) calcd for C\textsubscript{13}H\textsubscript{20}N\textsubscript{1}O\textsubscript{4}Br\textsubscript{1} 333.0576, found 333.0581; TLC \(R_f\) = 0.16 (ethyl acetate); Anal. Calcd for C\textsubscript{13}H\textsubscript{20}N\textsubscript{1}O\textsubscript{4}Br\textsubscript{1} C 46.71, H 6.03, N 4.19, found C 46.79, H 6.09, N 4.17.

3-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxymethyl}-5-trimethylsilanylethynyl-pyridine (6).

To a sealed tube was added 5 (3.595 g, 10.76 mmol), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (124.0 mg, 0.1768 mmol), and CuI (64.7 mg 0.340 mmol). The mixture was purged with argon for 5 min, and then triethylamine (20 mL) was added followed by dry and degassed trimethylsilylacetylene (7.75 mL, 54.9 mmol) and the mixture was heated in an oil bath at 80 °C. After 12 h the mixture was
diluted with CHCl$_3$ and aqueous NH$_4$Cl. The layers were separated and the aqueous phase was extracted with CHCl$_3$ (3 × 100 mL). The combined organic layers were washed with H$_2$O (200 mL) and dried over Na$_2$SO$_4$. The solvent was removed in vacuo to give a black oil. Purification by silica gel flash chromatography (ethyl acetate) gave 3.744 g (10.65 mmol, 99%) of 6 as a brown oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.59 (d, J = 1.8 Hz, 1H, 3), 8.48 (d, J= 2.1, 1H, 4), 7.75 (t, J = 2.0 Hz, 1H, 1), 4.55 (s, 2H, 6), 3.69-3.63 (m, 10H, 7-11), 3.54 (m, 2H, 12), 3.37 (s, 3H, 13), 0.25 (s, 9H, 16); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.7 (3), 148.0 (4), 138.1 (1), 133.2 (5), 120.0 (2), 101.4 (14), 98.3 (15), 71.9 (12), 70.6-70.5 (4 peaks, 6,8-10), 70.2 (11) 69.9 (7), 59.0 (13), -0.25 (16); EI MS (m/\text{v}) calcd for C$_{18}$H$_{29}$N$_1$O$_4$Si 351.1866, found 351.1881; TLC $R_f$ = 0.18 (ethyl acetate); Anal. Calcd for C$_{18}$H$_{29}$N$_1$O$_4$Si C 61.50, H 8.32, N 3.98, found C 61.54, H 8.34, N 4.07.

3-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxymethyl}-5-ethynyl-pyridine (7). To a solution of 6 (3.786 g, 10.77 mmol) was added a solution of tetrabutylammonium fluoride (TBAF) in THF (11.0 mL, 1.0 M). After 5 min the mixture was diluted with CHCl$_3$ and aqueous NH$_4$Cl. The layers were separated and the aqueous phase was extracted with CHCl$_3$ (3 × 100 mL). The combined organic layers were washed with H$_2$O (200 mL) and dried over Na$_2$SO$_4$. The solvent was removed in vacuo to give a black oil. Purification by silica gel flash chromatography (ethyl acetate) gave 2.510 g (9.155 mmol, 85%) of 7 as a brown oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.62 (d, J = 1.9 Hz, 1H, 3), 8.52 (d, J= 2.0, 1H, 4), 7.79 (t, J = 2.0 Hz, 1H, 1), 4.57 (d, J=0.5, 6), 3.70-3.63 (m, 10H, 7-11), 3.54 (m, 2H, 12), 3.36 (s, 3H, 13), 3.21 (s, 1H, 15); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.9 (3), 148.4 (4), 138.3 (1), 133.3 (5), 119.0 (2), 80.6 & 80.3 (14 & 15), 71.9 (12),
70.6-70.5 (4 peaks, 6.8-10), 70.1 (11) 70.0 (7), 59.0 (13); EI MS (m/ν) calcd for C₁₅H₂₁N₁O₄ 279.1471, found 279.1474; TLC R_f = 0.10 (ethyl acetate); HPLC (acetonitrile – 0.1% TFA in milliq water gradient) on a 2 cm × 2.1 mm Alltech Alltima C18 column (3 μM particle size and a flow rate of 350 μL/min) indicates 85% purity.

2-[2-(2-methoxyethoxy) ethoxy] ethyl 5-bromo-3-iodobenzoate. The synthesis of 2-[2-(2-methoxyethoxy) ethoxy] ethyl 5-bromo-3-iodobenzoate has been previous described and was performed here by a modified procedure.³ To a solution of 5-bromo-3-iodobenzoic acid (25.32 g, 77.45 mmol) and triethyleneglycol monomethyl ether (66.0 mL, 578 mmol) in toluene (100 mL) was added diphenylammonium triflate (2.474 g, 7.754 mmol). The reaction was refluxed at 120 °C for 21 h and the solvent was removed in vacuo. The mixture was then heated to 90 °C for 4 h in a Kugelrohr apparatus to remove the residual triethyleneglycol monomethyl ether. The black liquid was then twice purified by silica gel flash chromatography (hexanes/ethyl acetate 1/1) to give 34.7 g (73.3 mmol, 95 %) of 2-[2-(2-methoxyethoxy) ethoxy] ethyl 5-bromo-3-iodobenzoate as a yellow oil:¹H NMR (500 MHz, CDCl₃) δ 8.30 (t, J = 1.4 Hz, 1H, 5), 8.13 (dd, J= 1.7, 1.4 Hz, 1H, 1), 8.03 (dd, J = 1.8, 1.6 Hz, 1H, 3), 4.47 (m, 2H, 8), 3.82 (m, 2H, 9), 3.72-3.64 (m, 6H, 10-12), 3.54 (m, 2H, 13), 3.37 (s, 3H, 14); ¹³C NMR (126 MHz, CDCl₃) δ 163.8 (7), 143.8 (3), 137.2 (5), 133.2 (6), 132.0 (1), 123.0 (2), 94.0 (3), 71.9 (13), 70.6 (11), 70.6 (10,12) 69.0 (9), 64.8 (8), 59.0 (14); TLC R_f = 0.26 (hexanes/ethyl acetate 1/1).
2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-trimethylsilylethynyl benzoate. The synthesis of 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-trimethylsilylethynyl benzoate has been previously described and was performed here by a modified procedure. To a sealed tube was added 2-[2-(2-methoxyethoxy) ethoxy] ethyl 5-bromo-3-iodobenzoate (5.0140 g, 10.598 mmol), \( \text{PdCl}_2(\text{PPh}_3)_2 \) (381.3 mg, 0.5436 mmol), and CuI (216.8 mg 1.139 mmol). The mixture was purged with argon for 5 min, and then triethylamine (20 mL) was added followed by dry trimethylsilylacetylene (7.0 mL, 50. mmol). After 40 min the mixture was diluted with \( \text{CHCl}_3 \) and aqueous \( \text{NH}_4\text{Cl} \). The layers were separated and the aqueous phase was extracted with \( \text{CHCl}_3 \) (3 × 100 mL). The combined organic layers were washed with \( \text{H}_2\text{O} \) (200 mL) and dried over \( \text{Na}_2\text{SO}_4 \). The solvent was removed \textit{in vacuo} to give a black oil. Purification by silica gel flash chromatography (hexanes/ethyl acetate 1/4) gave 4.389 g (9.899 mmol, 93%) of 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-trimethylsilylethynyl benzoate as a yellow oil: \( ^1\text{H} \) NMR (500 MHz, \( \text{CDCl}_3 \)) \( \delta \): 8.10 (dd, \( J=1.8, 1.6 \text{ Hz} \), 1H, 1), 8.04 (t, \( J=1.5 \text{ Hz} \), 1H, 5), 7.77 (dd, \( J=1.8, 1.6 \text{ Hz} \), 1H, 3), 4.47 (m, 2H, 8), 3.82 (m, 2H, 9), 3.71-3.64 (m, 6H, 10-12), 3.53 (m, 2H, 13), 3.36 (s, 3H, 14), 0.25 (s, 9H, 17); \( ^{13}\text{C} \) NMR (126 MHz, \( \text{CDCl}_3 \)) \( \delta \): 164.6 (7), 138.6 (3), 132.5 (1), 131.9 (6), 131.7 (5), 125.4 (4), 122.0 (2), 102.2 (15), 97.2 (16), 71.9 (13), 70.6(10), 70.6 (11), 70.6 (12), 69.0 (9), 64.6 (8), 59.0 (14), -0.3 (17); TLC \( R_f = 0.17 \) (hexanes/ethyl acetate 1/4).
2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-ethynyl benzoate. The preparation of 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-ethynyl benzoate has been previously reported\(^4\) and was obtained as a yellow oil (99\%). The characterization data is consistent with the reported data, however peak assignments are provided here: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.16 (t, \(J=1.7\) Hz, 1H, 1), 8.09 (dd, \(J=1.4, 1.6\) Hz, 1H, 5), 7.80 (t, \(J=1.7\) Hz, 1H, 3), 4.48 (m, 2H, 8), 3.83 (m, 2H, 9), 3.72-3.65 (m, 6H, 10-12), 3.54 (m, 2H, 13), 3.37 (s, 3H, 14), 3.17 (s, 1H, 16); TLC \(R_f = 0.25\) (hexanes/ethyl acetate 1/1).

Br-A\(_2\)-Br (8). The synthesis of 8 has been previous described and was performed here by a modified procedure.\(^4\) To a sealed tube was added 2-[2-(2-Methoxyethoxy) ethoxy] ethyl 3-bromo-5-ethynyl benzoate (168 mg, 0.451 mmol), 2-[2-(2-methoxyethoxy) ethoxy] ethyl 5-bromo-3-iodobenzoate (220 mg, 0.465 mmol), \(\text{PdCl}_2(\text{PPh}_3)_2\) (18.8 mg, 0.0268 mmol), and CuI (15.4 mg 0.0809 mmol). The mixture was purged with argon for 5 min, triethylamine (2 mL) was
added, and the mixture was heated in an oil bath at 60 °C. After 11 h the mixture was diluted with CHCl₃ and aqueous NH₄Cl. The layers were separated and the aqueous phase was extracted with CHCl₃ (3 × 25 mL). The combined organic layers were washed with H₂O (100 mL) and dried over Na₂SO₄. The solvent was removed in vacuo to give a black oil. Purification by silica gel flash chromatography (hexanes/ethyl acetate 2/3) gave 268 mg (0.432 mmol, 96%) of 8 as a yellow oil: 

$$\begin{align*}
^1H \text{ NMR (}500 \text{ MHz, CDCl}_3) & \delta 8.17 (t, J=1.7 \text{ Hz}, 2H, 5), 8.13 (t, J=1.5 \text{ Hz}, 2H, 1), \\
& 7.85 (t, J=1.7 \text{ Hz}, 2H, 3), 4.50 (m, 4H, 8), 3.85 (m, 4H, 9), 3.73-3.65 (m, 12H, 10-12), 3.54 (m, 4H, 13), 3.36 (s, 6H, 14); \\
^13C \text{ NMR (}126 \text{ MHz, CDCl}_3) & \delta 164.5 (7), 138.3 9 (3), 132.9 (1), 132.2 (5), 131.5 (6), 124.6 (4), 122.3 (2), 88.9 (15), 71.9 (13), 70.6 (12), 70.6 (11), 70.6 (10), 69.0 (9), 64.7 (8), 59.0 (14); \\
\text{EI MS (m/v) calcd for } & \text{C}_{30}\text{H}_{36}\text{Br}_2\text{O}_{10} \text{ 714.0675, found 714.0675; TLC } R_f = 0.07 \text{ (hexanes/ethyl acetate 2/3).}
\end{align*}$$

**Pyr-A₂-Pyr (1).** Under an atmosphere of dry argon 8 (104 mg, 0.146 mmol), 7 (93.4 mg, 0.334 mmol), Pd(Pr-Bu)₂ (7.8 mg, 0.015 mmol), CuI (8.3 mg 0.044 mmol), and triethylamine (0.6 mL) were added to a vial. The vial was sealed with a Teflon lined cap then heated in an oil bath at 75 °C for 19 h. The mixture was diluted with CHCl₃ and filtered through celite. The solvent was removed in vacuo to give a dark yellow oil. Purification by silica gel flash chromatography (acetone/chloroform 1/9 → 3/2) gave 96.7 mg (0.0869 mmol, 60%) of 1 as a yellow oil: 

$$^1H \text{ NMR (}500 \text{ MHz, CDCl}_3) \delta 8.17 (t, J=1.7 \text{ Hz}, 2H, 5), 8.13 (t, J=1.5 \text{ Hz}, 2H, 1),$$

$$7.85 (t, J=1.7 \text{ Hz}, 2H, 3), 4.50 (m, 4H, 8), 3.85 (m, 4H, 9), 3.73-3.65 (m, 12H, 10-12), 3.54 (m, 4H, 13), 3.36 (s, 6H, 14);$$

$$^13C \text{ NMR (}126 \text{ MHz, CDCl}_3) \delta 164.5 (7), 138.3 9 (3), 132.9 (1), 132.2 (5), 131.5 (6), 124.6 (4), 122.3 (2), 88.9 (15), 71.9 (13), 70.6 (12), 70.6 (11), 70.6 (10), 69.0 (9), 64.7 (8), 59.0 (14);$$

$$\text{EI MS (m/v) calcd for } \text{C}_{30}\text{H}_{36}\text{Br}_2\text{O}_{10} \text{ 714.0675, found 714.0675; TLC } R_f = 0.07 \text{ (hexanes/ethyl acetate 2/3).}$$
NMR (500 MHz, CD$_3$CN) $\delta$ 8.70 (d, $J=1.9$ Hz, 2H, 20), 8.55 (d, $J=1.9$ Hz, 2H, 21), 8.20 (t, $J=1.6$ Hz, 2H, 5), 8.19 (t, $J=1.6$ Hz, 2H, 1), 7.99 (t, $J=1.6$ Hz, 2H, 3), 7.92 (t, $J=2.1$ Hz, 2H, 18), 4.59 (d, $J=0.4$ Hz, 4H, 23) 4.47 (m, 4H, 8), 3.81 (m, 4H, 9), 3.66-3.53 (m, 32H, 10-12,24-28), 3.46-3.42 (m, 8H, 13,29), 3.27 (s, 6H, 30), 3.24 (s, 6H, 14); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.5 (7), 151.4 (20), 148.3 (21), 138.3 (3), 137.8 (18), 133.5 (22), 132.7 (1), 132.7 (5), 131.0 (6), 123.5 (4,2), 119.4 (19), 90.5 (16), 88.9 (15), 87.5 (17), 71.9 (multiple peaks 13,30,45), 70.5-70.6 (6 peaks, 10-12,25-27), 70.2 (28), 70.0 (24), 69.0 (9), 64.5 (8), 60.0 (14), 60.0 (30); MALDI MS (m/ν) calcd for C$_{60}$H$_{76}$N$_{2}$O$_{18}$Na 1135.50, found 1134.80; GPC indicates >95% purity; TLC $R_f$ = 0.33 (acetone/chloroform 3/2).

TMS$\equiv-A_2\equiv$TMS. The preparation of TMS$\equiv-A_2\equiv$TMS has been previously reported and was obtained as a yellow oil (99%). The characterization data is consistent with the reported data, however peak assignments are provided here: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (t, $J=1.6$ Hz, 2H, 5), 8.10 (t, $J=1.6$ Hz, 2H, 1), 7.79 (t, $J=1.6$ Hz, 2H, 3), 4.50 (m, 4H, 8), 3.85 (m, 4H, 9), 3.73-3.65 (m, 12H, 10-12), 3.54 (m, 4H, 13), 3.36 (s, 6H, 14), 0.27 (s, 18H, 18); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.1 (7), 138.8 (3), 132.9 (6), 132.4 (1), 130.7 (5), 124.1 (4), 123.3 (2), 102.8 (16), 96.5 (17), 88.9 (15), 71.9 (13), 70.6 (12), 70.6 (11), 70.6 (10), 69.1 (9), 64.5 (8), 59.0 (14), -
0.23 (18); EI MS \((m/v)\) calcd for \(C_{40}H_{54}O_{10}Si_{2}\) 750.3256, found 750.3259; TLC \(R_f = 0.41\) (ethyl acetate).

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\begin{align*}
\text{H} \equiv \equiv \text{A}_2 \equiv \equiv \text{H} \ (9).
\end{align*}
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The preparation of 9 has been previously reported\(^4\) and was obtained as a yellow oil (69%). The characterization data is consistent with the reported data, however peak assignments are provided here: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.17 (t, \(J=1.6\) Hz, 2H, 5), 8.14 (t, \(J=1.6\) Hz, 2H, 1), 7.81 (t, \(J=1.6\) Hz, 2H, 3), 4.50 (m, 4H, 8), 3.85 (m, 4H, 9), 3.73-3.65 (m, 12H, 10-12), 3.54 (m, 4H, 13), 3.36 (s, 6H, 14), 3.16 (s, 2H, 17); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 165.0 (7), 138.9 (3), 133.2 (6), 132.9 (1), 130.9 (5), 123.4 (4), 123.1 (2), 88.8 (15), 81.6 (16), 79.0 (17), 71.9(13), 70.7 (12), 70.6 (11), 70.6 (10), 69.0 (9), 64.6 (8), 59.0 (14); EI MS \((m/v)\) calcd for \(C_{34}H_{38}O_{10}\) 606.2465, found 606.2447; TLC \(R_f = 0.25\) (ethyl acetate).
**Br-A_{4}-Br (10).** To a sealed tube was added 9 (259.8 mg, 0.428 mmol), 2-[2-(2-methoxyethoxy)ethoxy] ethyl 5-bromo-3-iodobenzoate (190.6 mg, 0.440 mmol), PdCl$_2$(PPh$_3$)$_2$ (16.6 mg, 0.0237 mmol), and CuI (18.0 mg 0.0945 mmol). The mixture was purged with argon for 5 min, and then triethylamine (1.5 mL) was added. After 18 h the mixture was diluted with CHCl$_3$ and aqueous NH$_4$Cl. The layers were separated and the aqueous phase was extracted with CHCl$_3$ (3 × 50 mL). The combined organic layers were washed with H$_2$O (100 mL) and dried over Na$_2$SO$_4$. The solvent was removed *in vacuo* to give a brown oil. Purification by silica gel flash chromatography (acetone/chloroform 1/4) gave 148.4 mg (0.114 mmol, 52%) of 14 as a yellow oil: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (t, J=1.6 Hz, 2H, 5), 8.19 (t, J=1.6 Hz, 2H, 1), 8.17 (t, J=1.7 Hz, 2H, 18), 8.15 (t, J=1.5 Hz, 2H, 22), 7.89 (t, J=1.6 Hz, 2H, 3), 7.87 (t, J=1.7 Hz, 2H, 20), 4.53 (m, 4H, 8), 4.51 (m, 4H, 25), 3.87 (m, 4H, 9), 3.85 (m, 4H, 26), 3.75-3.65 (m, 24H, 10-12,27-29), 3.54 (m, 8H, 13,30), 3.36 (s, 6H, 31), 3.35 (s, 6H, 14); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.0 (7), 164.5 (24), 138.4 (3,20), 132.9-132.8 (3 peaks, 1,5,22), 132.2 (18), 131.5 (23), 131.1 (6), 124.8 (19), 123.6 (4), 123.4 (2), 122.3 (21), 89.5 (16), 89.0 (15), 88.4 (17), 71.9 (13,30), 70.6 (multiple peaks, 10-12,27-29), 69.1 (26), 69.0 (9), 64.7 (25), 64.6 (8), 59.0 (14), 59.0 (31); MALDI MS (m/ν) calcd for C$_{62}$H$_{72}$Br$_2$O$_{20}$Na 1319.29, found 1319.24; GPC indicates >95% purity; TLC R$_f$ = 0.13 (acetone/chloroform 1/4).
**Pyr-A₄-Pyr (2).** To a sealed tube was added 10 (148.4 mg, 0.1144 mmol), 7 (87.1 mg, 0.312 mmol), Pd (P₄-Bu₅)₂ (9.0 mg, 0.018 mmol), and ZnBr₂ (379 mg 1.683 mmol). The mixture was purged with argon for 5 min, and then triethylamine (1.5 mL) was added. After 18 h the mixture was diluted with CHCl₃ and aqueous NH₄Cl. The layers were separated and the aqueous phase was extracted with CHCl₃ (3 × 50 mL). The combined organic layers were washed with H₂O (100 mL) and dried over Na₂SO₄. The solvent was removed *in vacuo* to give a brown oil. Purification by silica gel flash chromatography (acetone/chloroform 1/1) gave 102.5 mg (0.0605 mmol, 52%) of 2 as an off white waxy solid: ¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, J=1.9 Hz, 2H, 37), 8.55 (d, J=1.8 Hz, 2H, 36), 8.21-8.20 (m, 8H, 1,5,18,22), 7.90 (t, J=1.6 Hz, 2H, 3), 7.90 (t, J=1.6 Hz, 2H, 20), 7.85 (t, J=1.9 Hz, 2H, 34), 4.62 (s, 4H, 39), 4.53 (m, 8H, 8,25), 3.87 (m, 8H, 23), 3.75-3.64 (m, 44H, 10-12,27-29,40-44), 3.54 (m, 12H, 13,30,45), 3.36 (s, 6H, 46), 3.35 (s, 6H, 14), 3.34 (s, 6H, 31); ¹³C NMR (126 MHz, CDCl₃) δ 165.0 (7,24), 151.4 (36), 138.4 (37), 138.4 (32), 137.8 (34), 133.5 (38), 132.8-132.7 (4 peaks, 1,5,18,22), 131.1 (6), 121.0 (23), 123.6-123.5 (multiple peaks, 2,4,19,21), 119.5 (35), 90.6 (32), 89.0 (3 peaks, 15,16,17), 87.6 (33), 71.9 (13,30,45), 70.7-70.5 (multiple peaks, 10-12,27-29,39,41-43), 70.2 (44), 70.0
MALDI MS (m/z) calcd for C_{92}H_{112}N_{2}O_{28}Na 1716.73, found 1716.26; GPC indicates >95% purity; TLC R_f = 0.06 (acetone/chloroform 1/1).

**Br-Ae-Br (11).** To a sealed tube was added 9 (2.204 g, 3.076 mmol), Pd_2(dba)_3 (24.9 mg, 0.0272 mmol), PPh_3 (34.9 mg, 0.133 mmol), and CuI (11.5 mg 0.0604 mmol). The mixture was purged with argon for 5 min, and then triethylamine (15 mL) was added. The mixture was heated in an oil bath at 70 °C and during this time 8 (402.4 mg, 0.6633 mmol) dissolved in THF (8 mL) was added over the course of 3 h. After 40 h the mixture was diluted with ether and filtered through a celite plug. Aqueous NH_4Cl was added to the filtrate. The layers were separated and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic layers were washed with H_2O (200 mL) and dried over Na_2SO_4. The solvent was removed *in vacuo* to give a brown oil. Purification by silica gel flash chromatography (acetone/chloroform 1/9 → 3/7) gave 328.1 mg (0.1747 mmol, 26%) of 11 as a yellow oil: ^1^H NMR (500 MHz, CDCl_3) δ 8.20 (m, 6H, 5,1,18), 8.19 (t, J=1.6 Hz, 2H, 22), 8.17 (t, J=1.7 Hz, 2H, 38), 8.15 (t, J=1.5 Hz, 2H, 34), 7.89 (t, J=1.6 Hz, 2H, 3), 7.89 (t, J=1.6 Hz, 2H, 20), 7.87 (t, J=1.7 Hz, 2H, 36), 4.53 (m, 8H,
8.25), 4.50 (m, 4H, 41), 3.87 (m, 8H, 9,26), 3.85 (m, 4H, 42), 3.75-3.64 (m, 36H, 10-12,27-29), 3.53 (m, 12H, 13,30,46), 3.34 (s, 6H, 47), 3.34 (s, 6H, 14), 3.34 (s, 6H, 31); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.0 (7), 165.0 (24), 164.5 (24), 138.4 (3), 138.4 (20), 138.3 (36), 132.9-132.8 (4 peaks, 1,5,22,18), 132.1 (34), 131.5 (39), 131.1 (6), 131.1 (23), 124.8 (35), 123.6 (2), 123.6 (4), 123.6 (19) 123.4 (21), 122.3 (37), 89.5 (32), 89.0-88.9 (3 peaks 15-17), 88.4 (33), 71.9 (13,30,46), 70.6 (multiple peaks, 10-12,27-29,43-45), 69.0 (multiple peaks 9,26,42), 64.7 (41), 64.6 (8,25), 59.0 (multiple peaks 14,31,47); MALDI MS (m/v) calcd for C$_{94}$H$_{108}$Br$_2$O$_{30}$Na 1899.52, found 1899.42; GPC indicates >95% purity; TLC $R_f$ = 0.22 (acetone/chloroform 1/4).

**Pyr-A$_6$-Pyr (3).** Under an atmosphere of dry argon 11 (298.7 mg, 0.1591 mmol), 7 (108.2 mg, 0.3874 mmol), Pd(Pr-Bu)$_2$ (13.5 mg, 0.0264 mmol), Cul (2.5 mg 0.013 mmol), THF (2 mL), and triethylamine (2 mL) were added to a vial. The vial was sealed with a Teflon lined cap then heated in an oil bath at 70 °C for 42 h. The mixture was diluted with CHCl$_3$ and filtered through celite. The solvent was removed *in vacuo* to give a brown oil. Purification by silica gel flash chromatography (acetone/chloroform 1/1 → 9/1) gave 209.5 mg (0.0921 mmol, 58%) of 3 as an
off-white waxy solid: $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ 8.56 (d, J=1.8 Hz, 2H, 51), 8.43 (d, J=1.8 Hz, 2H, 50), 7.91 (d, J=1.6 Hz, 4H, 34,38), 7.86 (d, J=1.6 Hz, 4H, 18,22), 7.84 (d, J=1.5 Hz, 4H, 1,5), 7.73 (t, J=2.0 Hz, 2H, 53), 7.70 (m, 6H, 3,20,36), 4.48 (s, 4H, 55), 4.38 (m, 4H, 8), 4.38 (m, 4H, 25), 4.34(m, 4H, 41), 3.82 (m, 4H, 9), 3.80 (m, 4H, 26), 3.77 (m, 4H, 42), 3.70-3.53 (m, 44H, 10-12,27-29,43-45,56-60), 3.49-3.44 (m, 16H, 13,30,46,61), 3.28 (s, 6H, 62), 3.27 (s, 6H, 14), 3.27 (s, 6H, 31), 3.28 (s, 6H, 47); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.0 (7,24,40), 151.4 (51), 148.4 (50), 138.4 (3,20,36), 137.8 (53), 133.5 (54), 132.8-132.7 (multiple peaks, 1,5,18,22,34,38), 131.1-131.0 (multiple peaks, 6,23,39), 123.6-123.5 (multiple peaks, 2,4,19,21,35,37), 119.5 (52), 90.6 (48), 89.0 (multiple peaks, 15,16,17,32,33), 87.6 (49), 71.9 (13,30,46,61), 70.6-70.5 (multiple peaks, 10-12,27-29,43-45,55,57-59), 70.2 (60), 70.0 (56), 69.0 (9,26,42), 64.6 (8,25,41), 59.0 (14,31,47,62); MALDI MS (m/v) calcd for C$_{124}$H$_{148}$N$_2$O$_{38}$Na 2296.97, found 2297.66; GPC indicates >95% purity; TLC $R_f=0.19$ (acetone/chloroform 1/1).

1,4-Bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene. The preparation of 1,4-Bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene has been previously reported$^5$ and was obtained as a yellow oil (68%). The characterization data is consistent with the reported data, however peak assignments are provided here: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.82 (s, 4H, 1), 4.06 (m, 4H, 3), 3.81 (m, 4H, 4), 3.72 (m, 4H, 5), 3.67-3.64 (m, 8H, 6-7), 3.53 (m, 4H, 8), 3.36 (s, 6H, 9); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.0 (2), 115.4 (1), 71.8, 70.7, 70.6, 70.5, 69.8, 67.9, 59.0 (9); TLC $R_f=0.24$ (ethyl acetate).
1,4-Diiodo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]-benzene. The preparation of 1,4-Diiodo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]-benzene has been previously reported\textsuperscript{6} and was obtained as a yellow oil (56%). The characterization data is provided here: \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.22 (s, 2H, 1), 4.09 (m, 4H, 4), 3.87 (m, 4H, 5), 3.78 (m, 4H, 6), 3.68-3.66 (m, 8H, 7-8), 3.55 (m, 4H, 9), 3.37 (s, 6H, 10); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 153.0 (3), 123.4 (1), 86.3 (2), 71.9, 71.1, 70.7, 70.6, 70.2, 69.6, 59.0 (10); EI MS (\textit{m}/\textit{v}) calcd for C\textsubscript{20}H\textsubscript{32}I\textsubscript{2}O\textsubscript{8} 654.0187, found 654.0180; TLC \(R_f = 0.51\) (ethyl acetate). Anal. Calcd for C\textsubscript{20}H\textsubscript{32}I\textsubscript{2}O\textsubscript{8} C 36.71, H 4.93, N 0, found C 36.74, H 4.80, N 0.14.

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\text{2,5-bis-[(4-pyridinyl)-ethynyl]-1,4-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy]-benzene (12).}\]

To a sealed tube was added 1,4-Diiodo-2,5-bis-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene (843.7 mg, 1.290 mmol), 4-ethynylpyridine (431.7 mg, 3.093 mmol), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (78.7 mg, 0.112 mmol), and CuI (50.0 mg 0.263 mmol). The mixture was purged with argon for 5 min, and then triethylamine (5 mL) was added. After 12 h the mixture was diluted with CHCl\textsubscript{3} and aqueous NH\textsubscript{4}Cl and filtered through celite. The layers were separated and the aqueous phase was extracted with CHCl\textsubscript{3} (3 \times 75 mL). The combined organic layers were washed with H\textsubscript{2}O (100 mL), filtered through celite, and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed \textit{in vacuo} to give a brown oil. Purification by silica gel flash chromatography (acetone/chloroform 1/1) gave 148.4 mg (0.9671 mmol, 75%) of 12 as a white powder. \textit{Note: a solid sample of 12 decomposes upon exposure to light:} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.60 (dd,
J=4.4 Hz, J=1.7 Hz, 4H, 15), 7.37 (dd, J=4.5 Hz, J=1.2 Hz, 4H, 14), 7.06 (s, 1), 4.20 (m, 4H, 4), 3.92 (m, 4H, 5), 3.80 (m, 4H, 6), 3.66-3.60 (m, 8H, 7-8), 3.50 (m, 4H, 9), 3.34 (s, 6H, 10); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 153.8 (3), 149.8 (15), 131.2 (13), 125.3 (14), 117.3 (1), 113.9 (2), 92.4 (11), 90.0 (12), 71.8, 71.0, 70.7, 76.5, 69.6, 69.4, 59.0 (10); MALDI MS (m/v) calcd for C$_{34}$H$_{40}$N$_{2}$O$_8$ 604.2784, found 604.2785; TLC R$_f$ = 0.17 (acetone/chloroform 1/1). Anal. Calcd for C$_{34}$H$_{40}$N$_{2}$O$_8$ C 67.53, H 6.67, N 4.63, found C 67.70, H 6.75, N 4.64.

**Recovery of Oligomer from Supramolecular Complex.** Detailed below is a representative procedure for recovering free hexamer (2) from the palladium containing macrocycle; the same procedure works for each oligomer. To a 3 mL vial a stir bar, the supramolecular complex from 2 (20.0 mg, 10.6 µmol), PPh$_3$ (11.5 mg, 43.9 µmol), and acetone (2 mL) were added. The mixture was left to stir for 1 h. The resulting precipitate and solution were directly loaded onto a silica gel column. Purification by flash chromatography (acetone/chloroform 1/1) gave 9.2 mg (5.4 µmol, 51%) of 2 as an off white waxy solid.

**References**