Supporting Information

Supramolecular Chelation Based on Folding
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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 done under an atmosphere of dry 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. Dry triethylamine and acetonitrile were obtained using a solvent-purification system from Anhydrous Engineering. The $^1$H and $^{13}$C NMR spectra were recorded on a Varian Unity 400 or a Varian Unity 500 spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard (δ 7.24 ppm for CHCl$_3$). Coupling constants, $J$, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Mass spectra were obtained through the Mass Spectrometry Facility, School of Chemical Sciences, University of Illinois at Urbana-Champaign. Low resolution fast atom bombardment (FAB) mass spectra were obtained on a Micromass 70-VSE spectrometer. Matrix assisted laser desorption (MALDI) mass spectra were obtained using a Applied Biosystems Voyager-DE STR spectrometer.

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 GMHRH and 1x G3000H). Molecular weight data were determined using Viscotek’s TriSEC software. The light scattering, mass, and viscosity constants were determined from a single 90 kDa narrow polystyrene standard and checked against other known polystyrene standards for accuracy. TriSEC data were obtained in a solution of 89% tetrahydrofuran, 10% ehtanol, and 1 triethylamine at 30 °C. Conventional
calibration was performed with linear polystyrene standards.

All UV absorbance data were recorded with a Shimadzu (model UV-2501) spectrophotometer using either a 1.0 or 0.1 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 0.1 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 0.68 mM was loaded into the 250 µM automatic titration syringe. An initial injection of 4 µM was performed to remove any air bubbles. The remaining titrant was added in 24 injection of 10 µM each spaced 1500 seconds apart. 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 first and second binding of the oligomers with palladium were determined with the curve fitting program Origin form MicroCal inc. The stoichiometry of two oligomers for a single palladium was inputted into model.

**Nomenclature of Oligomers.** All oligomers dimer length and longer are designated using an abbreviated nomenclature system. The naming scheme follows the pattern: X-[A\textsuperscript{SC}]\textsubscript{n}-Y. End groups X and Y can indicate a, pyridine (Pyr), triazene (N\textsubscript{3}Et\textsubscript{2}), a bromide (Br), an iodide (I), trimethylsilylethynylene (≡-TMS), or an ethynylene group (≡-H). The substituent located between the two ethynyl groups is indicated by A, which would be directed inward when the oligomer assumes a helical conformation. The superscript SC indicate the side chain on the repeat unit, for instance triethylene glycol mono methyl ether attached to the repeat unit through an ester linkage is represented as CO\textsubscript{2}Tg. The number of repeat units is indicated by the subscript.
Synthesis.

**Pyr-[H\(^{\text{CO2Tg}}\)]-Br (9).** To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (86.0 mg, 0.094 mmol), copper iodide (18.5 mg, 0.097 mmol), triphenylphosphine (128.7 mg, 0.49 mmol), 7 (0.494 g, 4.78 mmol), and 8 (2.52 g, 5.33 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (25 mL) was added. The solution was degassed three times and allowed to react at 50 °C for 12 h. The mixture was concentrated in vacuo and purified by silica gel column chromatography (hexane/ethyl acetate, 2/3, 1/4) to give 1.31 g (2.93 mmol, 61%) of 9 as a light yellow oil: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.73 (s, 1H), 8.54 (d, \(J = 4.6\) Hz, 1H), 8.11 (t, \(J = 1.7\) Hz, 1H), 8.09 (t, \(J = 1.4\) Hz, 1H), 7.81 (t, \(J = 1.4\) Hz, 1H), 7.77 (dt, \(J = 4.0, 1.8\) Hz, 1H), 7.27 (dd, \(J = 8.1, 5.0\) Hz, 1H), 4.46-4.45 (m, 2H), 3.81-3.79 (m, 2H), 3.68-3.66 (m, 2H), 3.65-3.63 (m, 2H), 3.62-3.60 (m, 2H), 3.50-3.48 (m, 2H), 3.31 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 164.3, 152.2, 149.0, 138.4, 138.1, 132.6, 132.0, 131.2, 124.6, 123.0, 122.2, 119.4, 89.87, 88.96, 71.75, 70.49, 70.46, 68.86, 64.56, 58.87; FD MS (m/v) calcd for C\(_{21}\)H\(_{23}\)BrNO\(_5\) 448.1 (M+H), found 449.0; TLC \(R_f\) = 0.21 (hexane/ethyl acetate, 2/3).

**Pyr-[H\(^{\text{CO2Tg}}\)]≡-TMS (1).** To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (52.6 mg, 0.057 mmol), copper iodide (11.2 mg, 0.058 mmol), triphenylphosphine (72.7 mg, 0.27 mmol), and 9 (1.20 g, 2.68 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (12 mL) were added. The solution was degassed three times, charged with dry trimethylsilylethylnylene (0.75 mL, 1.1 g, 11 mmol), sealed, and allowed to react at 80 °C for 18 h. The mixture was
concentrated in vacuo and purified by silica gel column chromatography (hexane/ethyl acetate, 1/1) to give 1.21 g (2.59 mmol, 97%) of 1 as a light yellow oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$8.73 (s, 1H), 8.54 (d, $J$ = 4.8 Hz, 1H), 8.11 (m, 1H), 8.07 (m, H), 7.77 (m,1H), 7.26 (m, 1H), 4.47-4.45 (m, 2H), 3.82-3.80 (m, 2H), 3.69-3.67 (m, 2H), 3.69-3.67 (m, 2H), 3.65-3.60 (m, 4H), 3.50-3.48 (m, 2H), 3.32 (s, 3H), 0.22 (s, 9H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$164.9, 152.1, 148.9, 138.6, 138.4, 132.9, 132.3, 130.6, 124.0, 123.1, 123.0, 119.6, 102.7, 96.40, 90.57, 87.21, 71.77, 70.51, 70.49, 68.95, 64.40, 58.90, -0.30; FD MS (m/v) calcd for C$_{26}$H$_{32}$NO$_5$Si 466.2 (M+H), found 465.2; TLC $R_f$ = 0.20 (hexane/ethyl acetate, 3/1); Anal. Calcd for C$_{26}$H$_{31}$NO$_5$Si (465.20): C, 67.07, H, 6.71, N, 3.01. Found: C, 67.07, H, 6.63, N, 3.05.

**Pyr-[$\text{H}_{\text{CO}_2\text{Tg}}$]≡H (10).** To a solution of 1 (0.515 g, 1.11 mmol) in tetrahydrofuran (10 mL) was added a solution of tetrabutyl ammonium flouride in tetrahydr ofuran (1.2 mL, 1.0 M). The solution was allowed to react for 5 min then was concentrated in vacuo. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane, 1/3) to give 0.353 g (0.897 mmol, 81%) of 10 as a light yellow oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$8.70 (t, $J$ = 2.0 Hz, 1H), 8.50 (dd, $J$ = 4.9, 1.8 Hz, 1H), 8.10 (t, $J$ = 1.6 Hz, 1H), 8.06 (t, $J$ = 1.6 Hz, 1H), 7.75 (dt, $J$ = 8.1, 1.8 Hz, 1H), 7.74 (t, $J$ = 1.5 Hz, 1H), 7.23 (dd, $J$ = 7.8, 5.1 Hz, 1H), 4.44-4.42 (m, 2H), 3.79-3.77 (m, 2H), 3.66-3.64 (m, 2H), 3.62-3.57 (m, 4H), 3.47-3.45 (m, 2H), 3.28 (s, 3H), 3.15 (s, 1H); $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$165.07, 152.4, 149.2, 138.1, 138.8, 133.3, 133.0, 131.6, 123.5, 123.3, 123.2, 119.9, 90.71, 87.70, 81.78, 79.42, 72.06, 70.82, 70.78, 70.77, 69.21, 64.77, 59.18; FD MS (m/v) calcd for C$_{23}$H$_{23}$NO$_5$ 393.16 (M), found 393.1; TLC $R_f$ = 0.21 (hexane/ethyl acetate, 3/1).
Pyr-[H\(^{\text{CO}_2\text{Tg}}\)]\(_3\)-≡-TMS (2). To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (5.9 mg, 0.0064 mmol), copper iodide (1.7 mg, 0.0089 mmol), triphenylphosphine (4.7 mg, 0.018 mmol), 10 (48.5 mg, 0.123 mmol), and 12 (99.3 mg, 0.127 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (0.3 mL) and dry acetonitrile (1.5 mL) was added. The solution was degassed three times and allowed to react at 73 °C for 18 h. The mixture was concentrated in vacuo and purified by silica gel column chromatography (acetone/methylene chloride, 1/7, 1/5) to give 91.3 mg (0.087 mmol, 71%) of 2 as a light yellow oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.78 (d, \(J = 2.3\) Hz, 1H), 8.57 (dd, \(J = 4.9, 1.6\) Hz, 1H), 8.19-8.18 (m, 3H), 8.17 (t, \(J = 1.6\) Hz, 1H), 8.16 (t, \(J = 1.6\) Hz, 1H), 8.13 (t, \(J = 1.6\) Hz, 1H), 8.10 (t, \(J = 1.6\) Hz, 1H), 7.88 (t, \(J = 1.7\) Hz, 1H), 7.86-7.82 (m, 2H), 7.80 (t, \(J = 1.6\) Hz, 1H), 7.32 (dd, \(J = 8.0, 5.0\) Hz, 1H), 4.52-4.47 (m, 6H), 3.87-3.82 (m, 6H), 3.73-3.63 (m, 18H), 3.53-3.51 (m, 6H), 3.34-3.33 (m, 9H), 0.25 (s, 9H); FD MS (m/v) calcd for C\(_{58}\)H\(_{67}\)NO\(_1\)S\(_1\)Si 1045.43 (M+Na), found 1045.3; TLC \(R_f\) = 0.41 (acetone/methylene chloride, 1/4); GPC 1130 (M\(_n\)), 1.00 (M\(_w\)/M\(_n\)).

Pyr-[H\(^{\text{CO}_2\text{Tg}}\)]\(_3\)-≡-TMS (11). To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (8.8 mg, 0.0096 mmol), copper iodide (2.4 mg, 0.013 mmol), triphenylphosphine (8.3 mg, 0.031 mmol), 10 (72.0 mg, 0.183 mmol), and 12 (151.4 mg, 5.33 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (0.3 mL) and dry acetonitrile (2.0 mL) was added. The solution was degassed three times and allowed to react at 70 °C for 18 h. The mixture was concentrated in vacuo. The crude mixture was dissolved in tetrahydrofuran (5 mL) and a solution of tetrabutylammonium flouride in tetrahydrofuran (0.2 mL, 1.0 M) was added. The solution was allowed to react 5 min, diluted in methylene chloride (100 mL), washed with concentrated sodium bicarbonate (2 × 100 mL), dried with sodium sulfate, concentrated in vacuo, and purified by silica gel column chromatography (acetone/methylene chloride, 1/4, 2/3) to give 92.9 mg (0.095 mmol, 52%) of 11 as a light yellow oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.78 (d, \(J = 1.4\) Hz, 1H), 8.58 (dd, \(J = 4.8\),
1.6 Hz, 1H), 8.19-8.17 (m, 5H), 8.13 (t, J = 1.6 Hz, 1H), 7.89 (t, J = 1.5 Hz, 1H), 7.87-7.84 (m, 2H), 7.82 (t, J = 1.6 Hz, 1H), 7.33 (dd, J = 7.4, 4.2 Hz, 1H), 4.52-4.48 (m, 6H), 3.87-3.82 (m, 6H), 3.73-3.63 (m, 18H), 3.53-3.51 (m, 6H), 3.35-3.33 (m, 9H), 3.15 (s, 1H); FD MS (m/ν) calcd for C_{55}H_{59}NNaO_{15} 996.38 (M+Na), found 996.4; TLC R_f = 0.21 (acetone/methylene chloride, 1/4).

**Pyr-[H^{CO_2Tg}]_5≡TMS (3).** To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (5.9 mg, 0.0064 mmol), copper iodide (2.4 mg, 0.012 mmol), triphenylphosphine (5.0 mg, 0.019 mmol), 10 (41.4 mg, 0.105 mmol), and 13 (151.1 mg, 0.111 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (0.3 mL) and dry acetonitrile (1.5 mL) was added. The solution was degassed three times and allowed to react at 75 °C for 18 h. The mixture was diluted in methylene chloride (100 mL), washed with concentrated sodium bicarbonate (2 × 100 mL), dried with sodium sulfate, concentrated *in vacuo*, and purified by silica gel column chromatography (acetone/methylene chloride, 1/2) to give 122.4 mg (0.0753 mmol, 72%) of 3 as a thick light yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.56 (d, J = 3.8 Hz, 1H), 8.19-8.17 (m, 7H), 8.16 (t, J = 1.8 Hz, 1H), 8.13 (t, J = 1.6 Hz, 1H), 8.09 (t, J = 1.6 Hz, 1H), 7.89-7.88 (m, 3H), 7.86 (t, J = 1.6 Hz, 1H), 7.82 (dt, J = 8.0, 1.9 Hz, 3H), 7.80 (t, J = 1.6 Hz, 1H), 7.30 (dd, J = 7.8, 5.1 Hz, 1H), 4.52-4.47 (m, 10H), 3.87-3.82 (m, 10H), 3.73-3.62 (m, 30H), 3.52-3.50 (m, 10H), 3.33-3.32 (m, 15H), 0.24 (s, 9H); MALDI MS (m/ν) calcd for C₉₀H₁₀₃NNaO₂₅Si 1648.65 (M+Na), found 1649.20; TLC R_f = 0.31 (acetone/methylene chloride, 1/2); GPC 1530 (Mₙ), 1.01 (M_w/Mₙ).
**Pyr-[**H$^{\text{CO}_2\text{Tg}}$]**$_7$≡-TMS (4).** To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (4.0 mg, 0.0044 mmol), copper iodide (1.2 mg, 0.0063 mmol), triphenylphosphine (3.6 mg, 0.014 mmol), 11 (84.9 mg, 0.087 mmol), and 13 (125.9 mg, 0.092 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (0.3 mL) and dry acetonitrile (2.0 mL) was added. The solution was degassed three times and allowed to react at 70 °C for 12 h. The mixture was diluted in methylene chloride (100 mL), washed with concentrated sodium bicarbonate (2 × 100 mL), dried with sodium sulfate, concentrated in vacuo, and purified by silica gel column chromatography (acetone/methylene chloride, 3/7, 1/1) to give 145.2 mg (0.066 mmol, 76%) of 4 as a light yellow wax: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (dd, $J = 2.2$, 1.0 Hz, 1H), 8.58 (dd, $J = 5.3$, 1.8 Hz, 1H), 8.20-8.19 (m, 1H), 8.18 (t, $J = 1.7$ Hz, 1H), 8.16 (t, $J = 1.7$ Hz, 1H), 8.13 (t, $J = 1.6$ Hz, 1H), 8.09 (t, $J = 1.6$ Hz, 1H), 7.91-7.88 (m, 6H), 7.86 (t, $J = 1.7$ Hz, 1H), 7.80 (t, $J = 1.6$ Hz, 1H), 7.40-7.37 (m, 1H), 4.52-4.47 (m, 14H), 3.87-3.82 (m, 14H), 3.73-3.62 (m, 42H), 3.53-3.50 (m, 14H), 3.34-3.33 (m, 21H), 0.25 (s, 9H); MALDI MS ($m$/v) calcd for C$_{122}$H$_{139}$NNaO$_{35}$Si 2228.88 (M+Na), found 2231.01; TLC $R_f = 0.42$ (acetone/methylene chloride, 3/7); GPC 2520 (M$_n$), 1.01 (M$_w$/M$_n$).

**Pyr-[**H$^{\text{CO}_2\text{Tg}}$]**$_7$≡-TMS (5).** To a sealed tube fitted with a magnetic stirrer was added tris(dibenzylideneacetone)dipalladium (1.4 mg, 0.0015 mmol), copper iodide (1.1 mg, 0.0058 mmol), triphenylphosphine (1.3 mg, 0.0049 mmol), 10 (12.7 mg, 0.0323 mmol), and 14 (79.9 mg, 0.0317 mmol). The tube was evacuated and back filled with nitrogen three times and then dry triethylamine (0.3 mL) and dry acetonitrile (1.5 mL) was added. The solution was degassed three times and allowed to react at 70 °C for 18 h. The mixture was diluted in methylene chloride (100 mL), washed with concentrated sodium bicarbonate (2 × 100 mL), dried with sodium sulfate, concentrated in vacuo, and purified by silica gel column chromatography (acetone/methylene chloride, 3/7, 2/3, 1/1, 2/5) to give 51.6 mg (0.0185 mmol, 58%) of 5 as a light yellow wax: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 1H), 8.58 (d, $J = 4.1$ Hz, 1H), 8.20-8.17
(m, 15H), 8.16 (t, J = 1.6 Hz, 1H), 8.13 (t, J = 1.7 Hz, 1H), 8.09 (t, J = 1.6 Hz, 1H), 7.90-7.88 (m, 8H), 7.86 (t, J = 1.7 Hz, 1H), 7.80 (t, J = 1.6 Hz, 1H), 7.38 (b s, 1H), 4.52-4.46 (m, 18H), 3.87-3.81 (m, 18H), 3.73-3.61 (m, 54H), 3.52-3.49 (m, 18H), 3.34-3.31 (m, 27H), 0.24 (s, 9H); MALDI MS (m/ν) calcd for C154H175NNaO45Si 2809.11 (M+Na), found 2810.62; TLC Rf = 0.52 (acetone/methylene chloride, 2/3); GPC 3170 (Mn), 1.02 (Mw/Mn).

**Gel Permeation Chromatography of 1-5.** Traces were collected with a refraction index detector and were normalized to the same height.
**Structural search.** Cambridge Structural Database search of *trans*-dichlorobis(pyridine) palladium single crystal X-ray structure. Pyridines were considered to be *trans* if the N-Pd-N angle exceeded 170°. Dihedral angle \( \theta_1 \) and \( \theta_2 \) correspond to the separate planes of each pyridine aromatic rings, which were not necessarily coplanar as implied by the cartoon illustration. Search was performed on January 20, 2005 with ConQuest 1.7.
**Isothermal calorimetry data.** Collected at isothermal temperature of 20 °C. Each peak in titration curve corresponds to an injection.

Monomer 1:

\[ K_1 = 2.03 \pm 0.16 \times 10^5 \text{ M}^{-1} \]

\[ \Delta H_1^\circ = -7.82 \pm 0.07 \text{ Kcal mol}^{-1} \]

\[ K_2 = 3.30 \pm 0.20 \times 10^4 \text{ M}^{-1} \]

\[ \Delta H_2^\circ = -7.16 \pm 0.31 \text{ Kcal mol}^{-1} \]
Trimer 2:

$K_1 = 1.63 \pm 0.20 \times 10^5 \text{ M}^{-1}$

$\Delta H_1^\circ = -8.83 \pm 0.16 \text{ Kcal mol}^{-1}$

$K_2 = 7.36 \pm 0.77 \times 10^4 \text{ M}^{-1}$

$\Delta H_1^\circ = -6.08 \pm 0.42 \text{ Kcal mol}^{-1}$
Pentamer 3:
$K_1 = 5.84 \pm 0.34 \times 10^4 \text{ M}^{-1}$
$\Delta H_1^\circ = -7.33 \pm 0.53 \text{ Kcal mol}^{-1}$
$K_2 = 8.11 \pm 0.53 \times 10^5 \text{ M}^{-1}$
$\Delta H_1^\circ = -18.1 \pm 0.7 \text{ Kcal mol}^{-1}$
Heptamer 4:

\[ K_1 = 7.17 \pm 0.42 \times 10^4 \text{ M}^{-1} \]
\[ \Delta H_1^\circ = -9.24 \pm 0.96 \text{ Kcal mol}^{-1} \]

\[ K_2 = 2.81 \pm 0.11 \times 10^6 \text{ M}^{-1} \]
\[ \Delta H_2^\circ = -21.6 \pm 1.0 \text{ Kcal mol}^{-1} \]
Nonamer 5:

\[ K_1 = 4.40 \pm 0.33 \times 10^5 \text{ M}^{-1} \]

\[ \Delta H_1^\circ = -11.9 \pm 0.3 \text{ Kcal mol}^{-1} \]

\[ K_2 = 1.49 \pm 0.09 \times 10^6 \text{ M}^{-1} \]

\[ \Delta H_2^\circ = -11.9 \pm 0.3 \text{ Kcal mol}^{-1} \]