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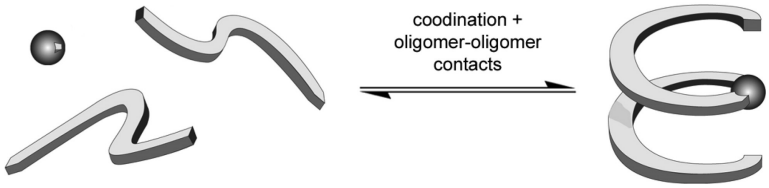

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Supramolecular Chelation Based on Folding

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Abstract: Crystallographic analysis revealed that pyridine−palladium complexation is a good geometric match to the *m*-phenylene ethynylene (*m*PE) repeat unit and thus could serve as a reversible linking group to join oligomer segments together. A series of pyridine-terminated *m*PE oligomers were then synthesized and found to coordinate with palladium dichloride to give complexes effectively twice the length of the free oligomers. A quantitative analysis of these coordination equilibria by isothermal calorimetry found the ability of the pyridine end-group to form a coordination complex corresponded with their ability to fold. Oligomers that were able to form complexes of sufficient length to fold showed positive cooperativity based on experimental determination of their association constants with a palladium ion. We suggest that the additional free energy of complexation for the folded oligomers is analogous to chelation by multidentate ligands, but here the "multidentate ligand" is held together by supramolecular rather than covalent bonds.

Introduction

Previous studies of *m*-phenylene ethynylene (*m*PE) oligomers have established that these chain molecules adopt a helical conformation in solution stabilized by multiple intrachain aromatic stacking interactions.[1−3] One of the reasons we and others[4−11] are interested in these artificial folding molecules or foldamers[12−17] is their potential for use as supramolecular catalysts,[18] and to this end we have begun incorporating functional groups into the interior cavity of the *m*PE helix.[19] Our recent demonstration of high alkylation rates in the interior of *m*PE oligomers confirms that substrate binding in the helix cavity enhances reactivity through a proximity effect.[20,21] This result also suggests that integration of a catalytic moiety into the structure of a *m*PE oligomer may impart desirable properties, such as substrate specificity since the cavity can bind molecules of different size and shape with varying association constants.[11,22,23] In addition, the inherently chiral environment provided by the helical structure[24] could prove useful for asymmetric transformations. Integration of a transition metal within the cavity of a *m*PE oligomer is one approach that we are currently pursuing to develop supramolecular catalysts. The focus of this report is to describe metal coordinating functionalities that are compatible with the folded state of *m*PE oligomers.

An earlier investigation of *m*PE molecules in which segments were joined through dynamic covalent bonds demonstrated that under equilibrium conditions shorter *m*PE chains are driven to form longer chains capable of adopting a stable helical conformation.[25,26] It seemed reasonable that two oligomers with coordinating end-groups could be joined with an appropriate metal to form a complex that was effectively twice the length of the individual strands. This approach is attractive since longer *m*PE oligomers chains are accessible in fewer synthetic steps and disassembly of the complex might be integrated into the catalytic cycle to facilitate turnover (i.e., by reducing product inhibition).

In contrast to traditional coordination complexes that are only stabilized by metal−ligand interactions, a *m*PE coordination

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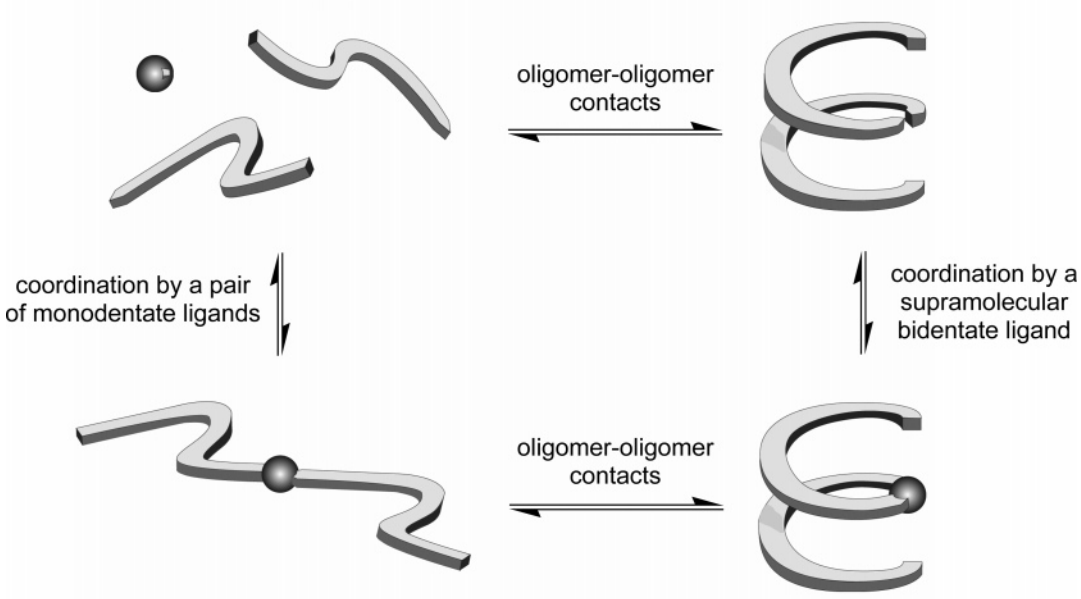
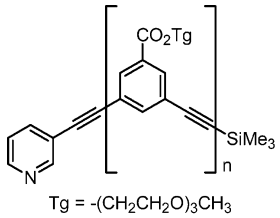


Figure 1. Metal coordination and oligomer−oligomer contacts through a highly compatible linkage share some of the same reductions in translational degrees of freedom upon formation of a folded coordination complex. This figure illustrates the concept of folding-based supramolecular chelation.

complex of sufficient length to fold would gain stability from both metal−ligand and interstrand oligomer−oligomer interactions. If both of these interactions are compatible, then they should share some of the same entropy costs due to their common loss of translational degrees of freedom. Thus, formation of the folded complex should incur a smaller entropic cost than would otherwise be realized if these events were uncoupled. In this way, positive cooperativity is realized, which within the context of metal−ligand coordination is analogous to a chelating effect.[27,28] Conventional chelating ligands have coordinating sites connected through covalent bonds; however, when folded and assembled, the two individual *m*PE monodentate ligands are noncovalently connected through multiple oligomer−oligomer contacts and thus behave as a supramolecular bidentate complex (Figure 1). We note that there have been reports of artificial DNA molecules containing metal coordinating base pairs, and these might also be considered to display a supramolecular chelating effect based on folding.[29,30]

Pyridine end-groups were investigated since complexation to a metal at an N−M−N angle of ca. 180° would provide a good match to the *m*PE backbone geometry. Similar pyridine-connected supramolecular coordination complexes have been described in the literature,[31−33] although it was the report of Lee et al.[34] that gave particular inspiration to us for this linkage. A palladium(II) metal ion provides stable coordination complexes in solution and is a good geometric match to the *m*PE backbone as detailed in the subsequent section. Following this lead, pyridine-terminated oligomers **1**−**5** were synthesized to



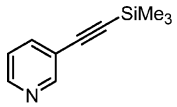
Tg = -(CH$_2$CH$_2$O)$_3$CH$_3$

1, n = 1
2, n = 3
3, n = 5
4, n = 7
5, n = 9

determine how chain length affects the ability of the oligomer to form a coordination complex. The influence of folding on the palladium−oligomer complexes was studied by UV absorption spectroscopy, ^{1}H NMR spectroscopy, and isothermal calorimetry. The systematic studies described below demonstrate that coordination of pyridine-terminated *m*PE oligomers with a palladium ion can be modulated by the propensity of the resulting complex to adopt a folded conformation.

Results and Discussion

Analysis of the Pyridine−Palladium(II)−Pyridine Coordination Group. To evaluate how well the coordination geometry of the pyridine−palladium complex matches the *m*PE backbone, pyridine end-group 3-trimethylsilylethynylpyridine **6**[35] was used as a model compound. Acetonitrile was chosen as



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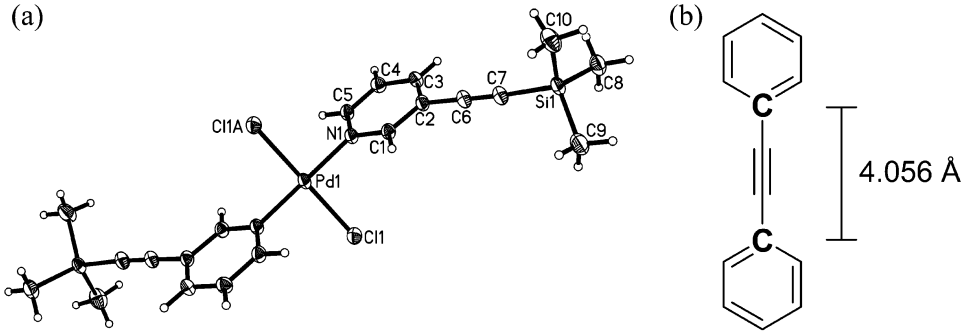

Figure 2. (a) Molecular structure of the palladium complex of **6**. Two benzene solvates are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level. (b) Average length between aromatic carbons of 283 diphenylacetylene structures found in the Cambridge Structural Database.

a solvent for these studies, as the helical conformation of *m*PE oligomers is stable and well understood in this solvent.[36] Since silver(I) coordinates with two pyridines at a bond angle of 180°, model compound **6** was first examined with 0.5 equiv of silver triflate in acetonitrile-d_3 by ^{1}H NMR spectroscopy. However, as might be expected, the silver complex was completely dissociated due to the coordinative character of acetonitrile that is in competition with the pyridine groups. Palladium(II) was then examined with the expectation that placement of pyridine ligands with a *trans* relationship in a square planar geometry would also give the desired bond angle of 180°. A ^{1}H NMR spectrum of **6** at a concentration of 2.8 mM in acetonitrile-d_3 with 0.5 equiv of *trans*-dichlorobis(acetonitrile)palladium indicated the formation of a complex in solution. New aromatic resonances downfield of those from uncomplexed **6** were observed. Information about the geometry of this coordination complex was then established by X-ray crystallographic analysis.

A palladium complex of **6** was prepared by mixing a solution of 3-trimethylsilylethynylpyridine **6** and *trans*-dichlorobis(acetonitrile)palladium in acetonitrile, and upon removal of solvent a yellow-orange microcrystalline solid was obtained. Crystals were then grown by slow diffusion of hexane into a solution of the complex in benzene. The resulting orange needle-shaped crystals were suitable for X-ray diffraction. Two benzene molecules crystallized with the complex, and the crystals were found to rapidly degrade in the absence of solvent. The molecular structure of the complex showed that the two pyridine rings were coplanar with the trimethylsilylethynyl groups directed away from each other in a transoid conformation (Figure 2a). With a distance of 4.032 Å between the pyridine nitrogens, the coordination complex was a good match to a phenylene ethylene repeat unit. This nitrogen-to-nitrogen distance was very close to the average distance of 4.056 ± 0.022 Å between the two ipso carbons of 283 diphenylacetylene structures obtained through a search of the Cambridge Structural Database (Figure 2b).[37]

An additional feature of the molecular structure was the chloride ligands that were directed above and below the plane of the pyridine rings. It is conceivable that these ligands might interfere with aromatic stacking in the folded conformation. A Cambridge Structural Database search identified 44 *trans*-dichlorobis(pyridine)palladium complexes and found no correlation between the length of the palladium−nitrogen bond and the position of the chloride ligands as determined by the dihedral angle, θ, between the average plane of the pyridine rings and the metal−ligand square coordinate plane (Figure 3).[37] These data suggest that the chloride ligands can probably rotate to an angle that would accommodate stacking interactions. The data further suggested that there is likely a limit to the dihedral angle since no such complexes were found for $\theta < 45°$. However, the observed range should provide sufficient conformational flexibility to allow incorporation of the coordination linker into folded oligomers without disruption of stacking. On the basis of the knowledge that was gained by analysis of the pyridine end-group, we then proceeded to synthesize pyridine-terminated *m*PE oligomers **1**−**5**.

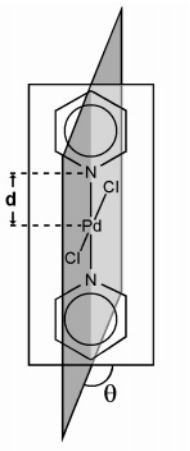

Figure 3. Illustration of palladium−nitrogen bond length and the dihedral angle between the plane of the pyridine rings and the metal−ligand coordination plane. Note that pyridine rings are not necessarily coplanar as implied by the illustration.

Synthesis. The synthesis of pyridine-terminated *m*PE oligomers **1**−**5** began from 3-ethynylpyridine **7**,[35] which was selectively coupled with 2-[2-(2-methoxyethoxy)ethoxy] ethyl 3-bromo-5-iodobenzoate **8** under Sonogashira conditions (Scheme 1).[38] The resulting compound **9** was then coupled with trimethylsilylacetylene to provide **1**. All longer lengths of pyridine-terminated oligomers were then derived from **1**. Removal of the trimethylsilyl group was accomplished by treatment with tetrabutylammonium fluoride to afford ethynylene-terminated **10** (Scheme 2).[39] The alkynyl group of **10** was then coupled to iodo-terminated dimer **12**, tetramer **13**, and octamer **14** to give

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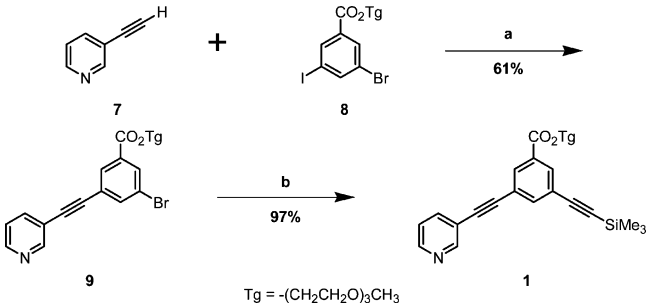
Scheme 1. Monomer **1** Synthesis[a]



[a] Reagents and conditions: (a) $Pd_2(aba)_3$, CuI, PPh_3, NEt_3, 70−80 °C. (b) trimethylsilylacetylene, $Pd_2(dba)_3$, CuI, PPh_3, NEt_3, 78−80 °C.

pyridine-terminated trimer **2**, pentamer **3**, and nonamer **5**, respectively. A portion of trimer **2** was treated with tetrabutylammonium fluoride to provide ethynyl-terminated trimer **11**. Trimer **11** was coupled with iodo-terminated tetramer **13** to yield pyridine-terminated heptamer **4**.

Palladium complexes were obtained by addition of 0.5 equiv of *trans*-dichlorobis(acetonitrile)palladium in acetonitrile to a solution of the pyridine-terminated oligomer in acetonitrile. Upon removal of solvent, the shorter oligomers **1**−**3** showed a visible physical change from a sticky oil to a pale white wax, which suggested formation of a higher molecular weight coordination complex. Oligomers **4** and **5** did not exhibit much physical change upon complexation; however, these compounds were a waxy substance prior to addition of the metal. These complexes were then studied by UV spectroscopy to probe their ability to fold.

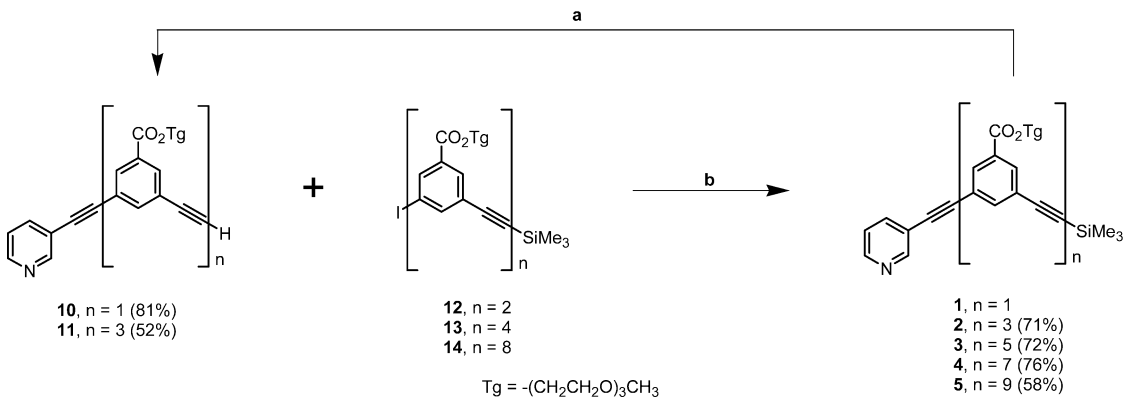
UV Absorption Spectroscopy. It has been established that the denatured and folded states of *m*PE oligomers have distinct UV absorption spectra.[1,2,7] A peak centered at 303 nm is present in the denatured conformation, while this feature is greatly attenuated when *m*PE oligomers adopt a folded structure. UV absorption spectroscopy was thus used to determine if folding is induced by metal−ligand coordination, consistent with the expectation advanced in Figure 1. Indeed the UV spectrum of palladium complex **3** in acetonitrile had a much smaller peak at 303 nm than the free oligomer (Figure 4). This is consistent with two pentameric oligomers linked by a palladium center that have adopted a folded conformation. In contrast, the UV spectrum of a complex prepared from **3** and 0.5 equiv of silver triflate closely resembled the spectrum of the free oligomer, suggesting that **3** did not coordinate strongly to the silver ion in acetonitrile and thus was unable to fold. This behavior is consistent with the ^{1}H NMR spectroscopic study mentioned above for trimethylsilylethynylpyridine **6**.

UV absorption spectra of palladium complex **3** were taken over a range of concentrations in acetonitrile (Figure 5). As the two components were diluted, a peak centered at 303 nm grew until the spectra resembled **3** alone. An isosbestic point is evident at 308 nm indicating a two-state equilibrium presumably between the folded and unfolded forms of **3**. Dilution probably destabilizes the helical conformation by disassociating the 2:1 oligomer-to-metal complex to give a mixture of the free oligomer and the 1:1 oligomer-to-metal complex. Both components of this mixture are too short to assume a folded conformation and therefore would account for the peak centered at 303 nm.

Strong evidence that the metal ion is linking two separate *m*PE chains to form a folded structure in solution was obtained by comparing different lengths of pyridine-terminated oligomers. Previous studies found that *m*PE oligomers composed of eight repeat units or less are not capable of folding.[1,2] The 2:1 palladium complexes of pentamer **3**, heptamer **4**, and nonamer **5** are composed of 12, 16, and 20 aromatic units including the terminal pyridine groups, respectively, and therefore should be capable of folding. UV spectra of palladium complexes of **1**−**5** confirmed this hypothesis, as only the spectra of **1** and **2** had a strong absorption peak centered at 303 nm (Figure 6). This chain length dependent spectroscopic signature suggests **1**−**5** form 2:1 oligomer-to-metal complexes in solution that are effectively twice the length of the free oligomer and have the ability to adopt a folded conformation. An NMR study of the pyridine-terminated oligomers was then undertaken to gain an understanding of the molecular species involved in the equilibria of these complexes.

NMR Spectroscopy. Further evidence for the folding of metal coordination complexes was obtained through a ^{1}H NMR spectroscopic titration of monomer **1** and pentamer **3** with palladium. ^{1}H NMR spectra of both pyridine-terminated oligomers **1** and **3** were collected at a concentration of 1 mM in acetonitrile-d_3 with varying equivalents of *trans*-dichlorobis(acetonitrile)palladium. For both **1** and **3**, the concentration of free oligomer (resonances highlighted yellow in Figure 7) was observed to decrease upon addition of palladium. For monomer **1** this decrease in the free oligomer corresponded to the appearance of a new set of resonances just downfield of free **1** that were assigned to the 2:1 complex as this species reached a

Scheme 2. Synthesis of Pyridine-Terminated MPE Oligomer Series[a]



[a] Reagents and conditions: (a) TBAF, THF (b) $Pd_2(dba)_3$, CuI, PPh_3, NEt_3, CH_3CN, 78−80 °C.

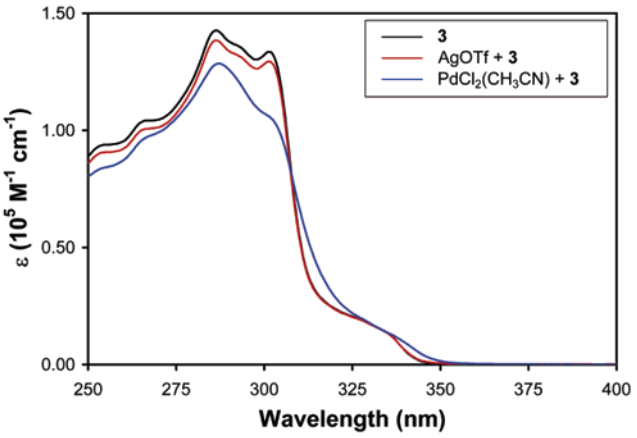


Figure 4. UV spectra of a 100 μM solution of **3** without any metal, a palladium complex of **3**, and a silver complex of **3** in acetonitrile at room temperature (see key inset). The molar extinction coefficient was calculated on the basis of the concentration of **3**.

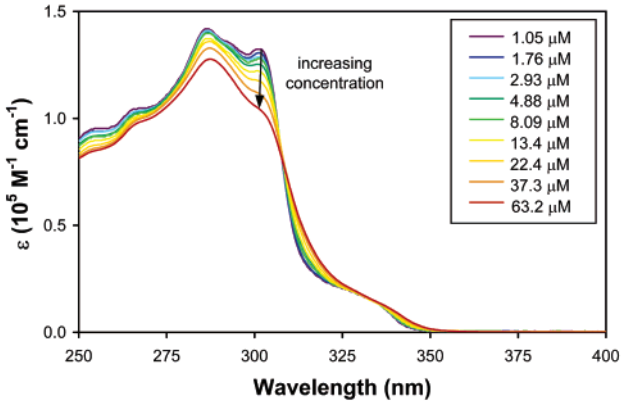


Figure 5. UV spectra of palladium complex **3** at various concentrations in acetonitrile obtained at room temperature. The indicated concentration corresponds to **3**.

maximum concentration at 0.50 equiv of palladium (resonances highlighted blue in Figure 7). Pentamer **3** had a greatly broadened signal at 0.50 equiv of palladium, consistent with ^{1}H NMR spectra of helically folded *m*PE oligomers observed in previous studies.[1] At higher concentrations of palladium with **1** and **3** a new set of peaks were found just upfield of the 2:1 complex, and these were assigned to the 1:1 complex (resonances highlighted red in Figure 7). Relatively sharp resonance peaks for this species in the ^{1}H NMR spectra of **3** support this assignment since the 1:1 complex consists of only a pentamer and thus is to short to fold.

Qualitatively, the difference between the two oligomers is striking. For monomer **1**, all three species are simultaneously observable at 0.50 equiv of palladium, while for pentamer **3**, neither the free oligomer nor the 1:1 complex is observed under these conditions. At 3.0 equiv of palladium, ca. 84% of monomer **1** exists as the 1:1 complex, while under these same conditions less than a third of pentamer **3** was present as a 1:1 complex. The behavior of **3** is strongly indicative of positive cooperativity. Stabilization of the 2:1 complex for **3** relative to **1** must be provided by chain−chain contacts present in the folded helical conformation. To gain a more quantitative understanding of the energetics that influence these equilibria, isothermal calorimetry was employed.

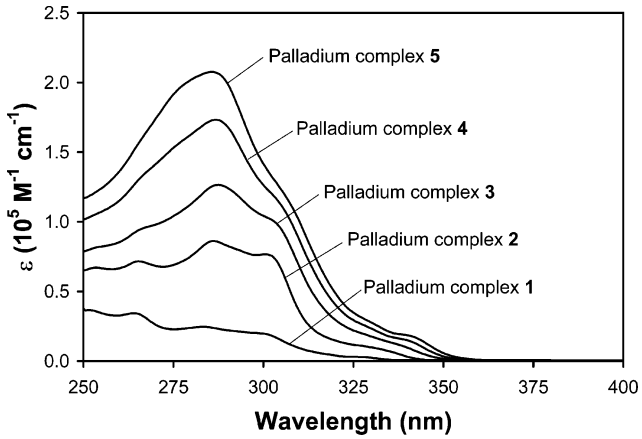


Figure 6. UV spectra of palladium complexes **1**−**5** at ca. 80 μM in acetonitrile at room temperature. The molar extinction coefficient was calculated on the basis of the concentration of oligomer.

Isothermal Calorimetry. Isothermal calorimetry is a powerful tool that allows direct measurement of the heats of reaction. Considering that the pyridine end-groups on oligomers **1**−**5** have nearly identical local steric and electronic characteristics, thermodynamic differences between them should correlate with their ability to fold. Solutions of **1**−**5** were prepared at 0.10 mM in acetonitrile and titrated with a 0.68 mM solution of *trans*-dichlorobis(acetonitrile)palladium in acetonitrile (Figure 8). After subtracting the heat of dilution, the data were fit to a sequential binding model in which the association constants are defined by the number of oligomers bound to a single metal center. The number of binding sites was set equal to two, and the binding affinities (K_1, K_2) and binding enthalpies (ΔH_1, ΔH_2) for coordination of the first and second oligomer to the metal were obtained from this analysis. From these values the free energy and entropy of the individual steps were calculated. The thermodynamic parameters obtained were found to correspond with the ability of **1**−**5** to form complexes capable of folding (Table 1).

$$\mathrm{M} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{ML}$$

$$\mathrm{ML} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{ML_2}$$

The overall free energy for the complexation of pyridine-terminated oligomers **1**−**5** with palladium became more negative with increasing chain length, which is anticipated since longer oligomers will have greater contact between coordinated chains (Figure 9). The free energy of complexation was approximately linearly dependent on chain length with the exception of monomer **1**. Deviation of **1** from linearity might be explained by considering that complexes of **1** and **2** are not able to fold and therefore no additional energy is gained through interchain contacts, in contrast to longer oligomers. The slightly greater overall free energy of **2** could arise from nonspecific interchain contacts between coordinated oligomers not available to complexes of **1**. Analyses of the entropic and enthalpic contribution to the overall free energy provide no further insight since the divergence between values for **1** and **2** remains within the range of error.

There were, however, significant differences in the enthalpy and entropy trends for oligomers **3**−**5**. We suggest that these differences can be understood by considering the oligomer's ability to form coordination complexes capable of folding. It is

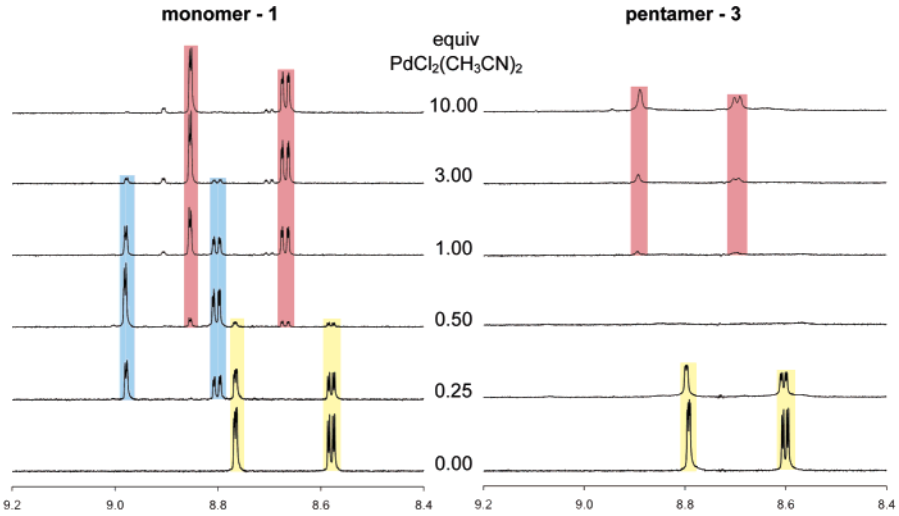


Figure 7. ^{1}H NMR spectra of 1 mM monomer **1** and pentamer **3** with varying equiv of $PdCl_2(CH_3CN)_2$ in CD_3CN at 19.6 °C. Resonances colored as follows: free ligand (yellow), 2:1 complex (blue), and 1:1 complex (red). Peaks are normalized to a mesitylene internal standard.

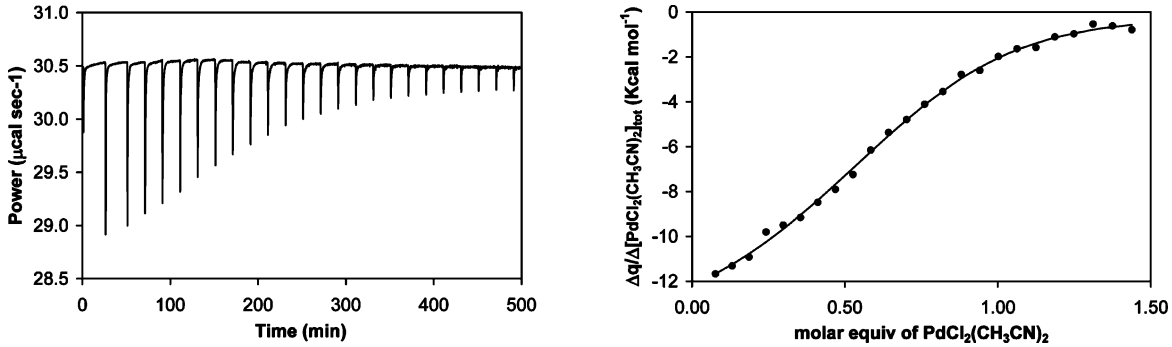


Figure 8. Typical isothermal calorimetry titration curves of **1** with $PdCl_2(CH_3CN)_2$ (right) and integrated profile with fit (left).

Table 1. Thermodynamic Parameters for **1**−**5** Binding to $PdCl_2(CH_3CN)_2$ in Acetonitrile at 20 °C

	1	2	3	4	5
$\Delta G°$ (kcal mol^{-1})	−13.2 ± 0.1	−13.5 ± 0.1	−14.3 ± 0.1	−15.2 ± 0.1	−15.9 ± 0.1
$\Delta H°$ (kcal mol^{-1})	−15.0 ± 0.3	−14.9 ± 0.5	−25.4 ± 0.8	−30.8 ± 1.4	−23.8 ± 0.4
$T\Delta S°$ (kcal mol^{-1})	−1.8 ± 0.3	−1.4 ± 0.5	−11.1 ± 0.8	−15.7 ± 1.4	−8.0 ± 0.4

useful to frame the analysis of the thermodynamic data with the knowledge that there are six repeat units in a single turn of folded helical *m*PE olgiomers as was previously established through a spin-labeling study.[3] There is an increase in overall enthalpy of complexation of pentamer **3** that can be explained by formation of ca. six new aromatic−aromatic contacts upon coordination of two oligomers to a single palladium metal center (Figure 10). The enthalpic gain for **3** is largely offset by a higher cost in entropy that probably arises from restricted rotation of eight single bonds between the ethynyl and phenylene units and the pyridine rings coordinated to palladium of the folded complex. This entropic cost results in a smaller overall gain in free energy. The behavior of pentamer **3** and longer oligomers **4** and **5** is consistent with entropy−enthalpy compensation.[40−42] The enthalpy of complexation was even greater for heptamer **4**, consistent with the formation of ca. eight new aromatic−aromatic contacts upon formation of a coordination complex. This increase in enthalpy is offset by a greater entropic cost that might be attributed to the restricted rotation of thirteen single bonds between the ethynyl and phenylene units as well as the pyridine rings coordinated to palladium in the folded conformation. However, the entropy cost of **4** did not completely offset the enthalpic gain, leading to a drop in free energy. The trend in overall free energy of complexation continues for nonamer **5**. However, **5** is long enough to fold prior to complexation with palladium. Thus, nonamer **5** has a lower enthalpy of complexation than heptamer **4**, as it only gains ca. six new aromatic−aromatic contacts when the ends of the folded helices meet upon coordination to palladium. Nonetheless, nonamer **5** has a greater overall free energy due to a smaller change in entropy. The smaller entropic cost is also consistent with a folded conformation of **5** prior to coordination with palladium since most of the entropic cost of complexation is assumed by the uncoordinated ligands. Therefore folding of the coordination complex restricts the rotation of only two additional single bonds between the ethynyl and phenylene units along with the pyridine rings coordinated to palladium.

Further insight was gained by examining individual thermodynamic parameters for complexation of the first and second oligomers to the palladium ion. Association constants of the metal with the first oligomer (K_1) and with the second oligomer (K_2) vary with their ability to form folded complexes. For oligomers **1** and **2**, which are unable to form folded complexes, K_1

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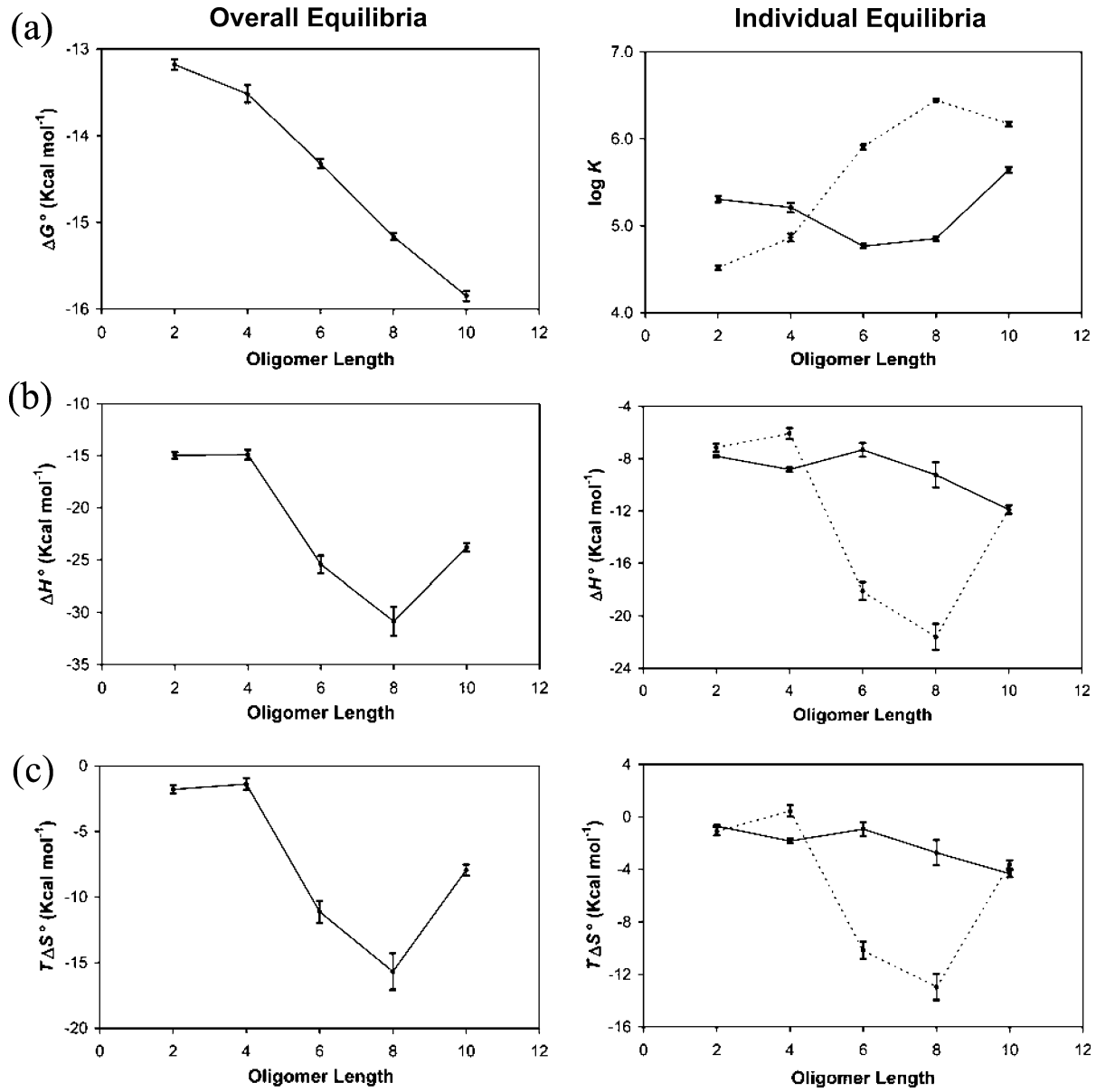

Figure 9. Thermodynamic parameters for binding of **1**−**5** with $PdCl_2(CH_3CN)_2$ obtained by fitting calorimetric data to a sequential binding model. Overall thermodynamic value of complexation (left) and individual values for the first and second oligomer complexations (right) are plotted. (a) Free energy of complexation and individual association constants K_1 (solid line) and K_2 (dotted line) displayed as a function of chain length. (b) Total enthalpy of complexation $\Delta H°$ and individual enthalpies $\Delta H_1°$ (solid line) and $\Delta H_2°$ (dotted line) displayed as a function of chain length. (c) Total entropy of complexation $T\Delta S°$ and individual entropies $T\Delta S_1°$ (solid line) and $T\Delta S_2°$ (dotted line) displayed as a function of chain length. Oligomer length defined as the number of aromatic rings per oligomer.

is greater than K_2, as would be expected due to the *trans* influence of the first pyridine end-group that lowers the association constant of the second pyridine end-group relative to acetonitrile.[43] Oligomers **3**−**5**, which are of sufficient length to form folded complexes, overcome *trans* influence and K_2 is actually greater than K_1. Thus we suggest that the positive cooperativity exhibited by the longer oligomers is analogous to a chelating effect.[44,45] The enthalpic and entropic contributions to complexation of the first oligomer with the metal ion show relatively small variation with chain length, consistent with exclusive formation of a new metal−oligomer coordination interaction. In contrast, complexation of the second oligomer varies greatly in enthalpy and entropy with chain length and follows a trend similar to the overall complexation described above.

Nonamer **5** requires further explanation since the enthalpies and entropies for the first and second complexations are nearly identical within experimental error. One might reasonably expect complexation of the second oligomer to be greater than the first as it gains additional oligomer−oligomer contacts upon joining together the ends of the folded helices. However, this is not consistent with the data, and we therefore suggest that the interchain contributions to the free energy of complexation are present prior to coordination with the palladium ion possibly in an aggregated state of the folded oligomer. Evidence for aggregation of *m*PE oligomers has been found in previous studies.[46] This aggregated state might be thermodynamically equivalent to the supramolecular bidentate proposed in Figure

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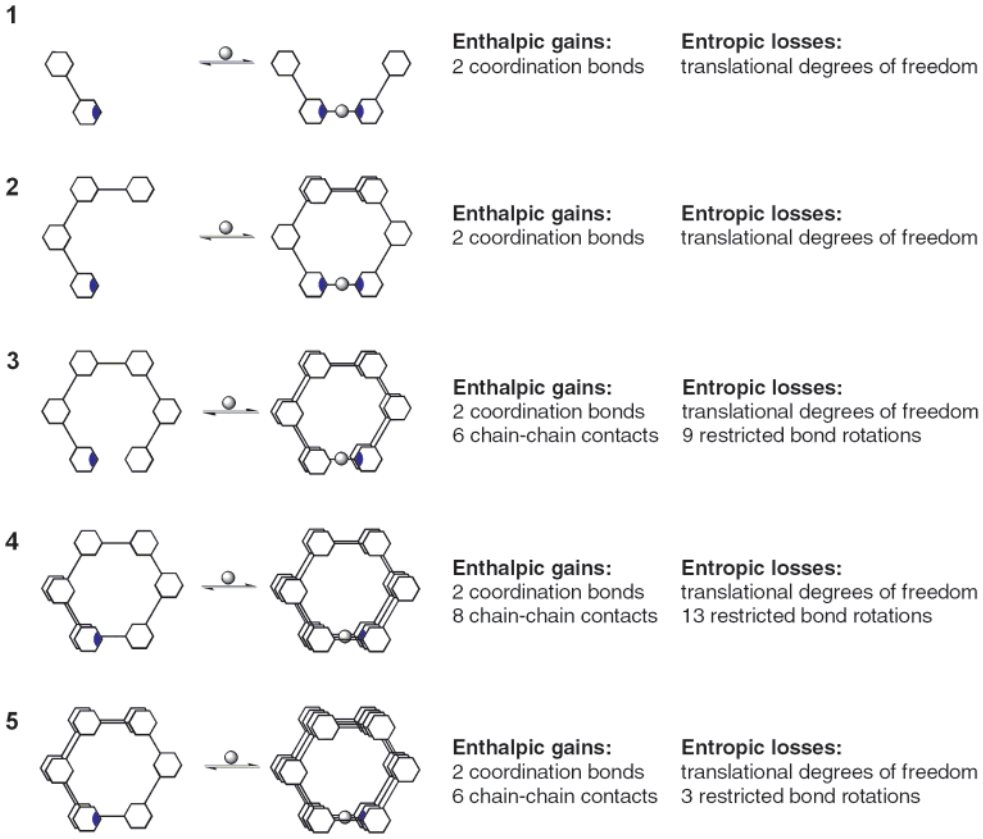

Figure 10. Simplified model of the thermodynamics of complexation that includes enthalpic and entropic contributions as they vary with chain length. Note that oligomers composed of eight repeat units are not capable of folding, although they appear to gain some nonspecific contacts, and also note that rotation of end-groups is not restricted upon assumption of a folded conformation.

1 in which the oligomer−oligomer interactions are gained prior to coordination. For such a case the enthalpy and entropy of the individual equilibria are primarily due to the coordination of the pyridine end-groups with palladium and should therefore be nearly equivalent.

Despite the fact that the overall free energy for complexation of pyridine-terminated oligomers **1**−**5** displays a nearly linear dependence on chain length, the individual equilibria can be most simply explained by considering the degree to which the free oligomer, 1:1 complex, and 2:1 complex are folded. This is reasonable since the coordinating pyridine end-groups on oligomers **1**−**5** have nearly identical local steric and electronic characteristics; therefore, thermodynamic differences between them can be attributed to their ability to fold. We suggest that the additional free energy of complexation for the folded oligomers is analogous to chelation by multidentate ligands, but here the "multidentate ligand" is held together by supramolecular rather than covalent bonds.

Conclusions

A series of pyridine-terminated *m*PE oligomers was synthesized and found to coordinate with *trans*-palladium dichloride, giving complexes effectively twice the length of the free oligomer. Those oligomers that were able to fold upon coordination with palladium displayed positive cooperativity. This study lays the foundation for further investigations of transition metal complexes that are capable of catalyzing reactions at room temperature in acetonitrile within the helical cavity. This will likely require modification of the oligomer's coordinating groups to obtain a catalytically active complex that is compatible with the folded conformation of the *m*PE oligomer. The understanding gained through this study will help to achieve this objective.

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Supporting Information Available: Experiment procedures of the synthesis of compounds **1**−**5** and their precursors, plot showing correlation of parameters for pyridine−palladium complexes obtained through search of the Cambridge Structural Database, raw and integrated ITC data with fit, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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