Experimental Section

PSS ($M_W = 70000$ Da) and PAH ($M_W = 70000$ and 15000 Da) were obtained from Aldrich. Silica particles (50 nm) were prepared according to the method reported by Stöber et al.[7] MF particles (3.99 μm) were purchased from Microparticles GmbH, Germany.

The procedure employed for the deposition of PSS, PAH, silica, and PAH-coated silica nanoparticles onto the surface of MF microparticles is as follows: A solution (1.5 mL) of the species with a charge opposite to that of the MF templates or the last layer deposited (1 mg mL^{-1} PSS or PAH in 0.5 M NaCl or 2 wt% silica or PAH-coated silica nanoparticles in 0.1 N NaCl) was added to a template latex solution (0.3 mL) and left to adsorb for 15 min. The excess added species was removed after each layer was deposited by centrifugation (2000 g, 2 min)/washing/redispersion cycles (× 3) with dilute aqueous NaCl. After the final washing step, the particles were redispersed in water (0.3 mL). Subsequent layers were deposited until the desired number of multilayers was achieved. Silica particles (50 nm) were covered with one PAH layer by using a similar procedure except that centrifugation (10000 rpm, 10 min) was used for the particle separation. Hollow capsules were prepared by dissolving the MF cores with 0.1 M HCl solution. Silica particles in the walls of the capsules were removed with 0.1 M HF solution.

Confocal micrographs were taken with a confocal laser scanning microscope "Aristoplan" from Leica (Germany) equipped with a 100 × oil immersion objective.

The morphology of the capsule wall was investigated by transmission electron microscopy of ultrathin sections. The sections were made on an ultramicrotom "Ultracut E" after embedding them in a mixture of methyl methacrylate and *n*-butyl methacrylate. The sections were observed through a Zeiss EM 902 transmission electron microscope.

Received: April 5, 2002
Revised: July 15, 2002 [Z19050]

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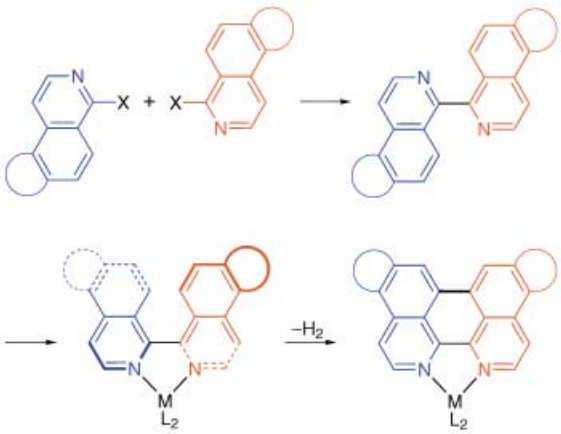
Ru^{II} Complexes of "Large-Surface" Ligands**

Edith C. Glazer and Yitzhak Tor*

Ru^{II}–polypyridyl complexes have traditionally been synthesized by a complexation reaction of the ligand of interest with the appropriate Ru^{II} precursors.[1] Although significant advances have been made in synthesizing modified 2,2′-bipyridine-, 1,10-phenanathroline-, and 2,2′:6,2″-terpyridine-type ligands, these methodologies provide access to a rather constrained set of structural motifs.[2] In particular, the range of Ru^{II} complexes that contain large, extended surfaces is limited,[3] despite their enormous potential as nucleic acid intercalators, luminescent probes, as well as energy and electron donors and acceptors.[4,5] We envisage a new methodology for the fabrication of extended polypyridyl systems from modular building blocks by the dehydrogenation reaction of a strained metal-complexed ligand (Scheme 1).[6,7]



Scheme 1. Extended symmetric and asymmetric bipyridine-type ligands are synthesized in a modular fashion from simpler heterocycles. The chelating ligand is enforced into a *syn* orientation within an octahedral complex and can then undergo a dehydrogenation reaction to a planar "large-surface" metal–polypyridine complex.

In this modular approach, nitrogen-containing heterocycles are homo- or heterocoupled to give extended bipyridines that can subsequently be coordinated and dehydrogenated to give the desired coordination complexes (Scheme 1).[8] Here we report the successful implementation of this strategy for the preparation of biologically active eilatin-containing complexes as well as Ru^{II} complexes of previously unknown "large-surface" ligands.

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[**] We thank the National Institutes of Health (Grant No. GM 58447) for generous support. We are grateful to Dr. Moshe Kol for authentic samples of eilatin-containing complexes.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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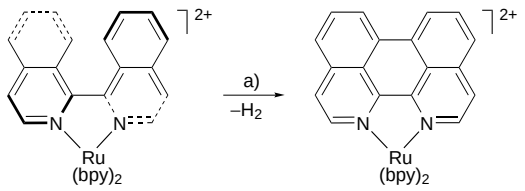
The 1,1′-biisoquinoline-containing Ru^{II} complex (**1**) was selected as a model system for exploring the dehydrogenation procedure (Scheme 2). This coordination compound is easily



1 **2**

Scheme 2. Dehydrogenation of $[Ru(bpy)_2(1,1'\text{-biisoquinoline})]^{2+}$ (**1**) to $[Ru(bpy)_2(1,12\text{-diazaperylene})]^{2+}$ (**2**). Reagents and conditions: a) Pd/C, ethylene glycol–acetone 10:1, 175–195 °C, 24 h, 30 % yield. All complexes were isolated as their PF_6^- salts.[10]

prepared by treating $[Ru(bpy)_2Cl_2]$ (bpy = 2,2′-bipyridyl) with the known biisoquinoline ligand.[9] Heating a solution of complex **1** in ethylene glycol with preactivated Pd/C to 175–195 °C for 24 h leads to the formation of complex **2** (30 % yield), which contains the fused 1,12-diazaperylene ligand.[10] This "subtle" transformation can be monitored by spectroscopic techniques. The presence of distinct, slowly interconverting diastereomeric complexes of the unfused coordination compound **1**[11] results in complicated ^1H and ^{13}C NMR spectra that are simplified upon dehydrogenation to the racemic product **2** (Figure 1 a). Additionally, fusing the two isoquinoline rings results in dramatic changes in the UV/Vis absorption spectrum. Characteristic transitions, particularly the visible metal-to-ligand charge-transfer (MLCT) bands, are significantly shifted to longer wavelengths (Figure 1 b). Cyclic and square-wave voltammetry measurements further support the planarization of the biisoquinoline moiety in **1** to the diazaperylene core in **2**. While the metal-centered $Ru^{3+/2+}$ wave remains essentially unchanged ($E_{1/2} = 1.28$ V versus a saturated calomel electrode (SCE)),[12] the first two reduction waves in **2** show a significant shift to lower potentials when compared to **1** ($\Delta E_{1/2} \geq 0.2$ V), as anticipated for the dehydrogenated product (Figure 1 c). Final confirmation of the successful dehydrogenation of **1** into **2** is obtained by mass spectrometry and by synthesizing an authentic sample of **2** by an independent synthetic route.[13] It is important to note that the free 1,1′-biisoquinoline ligand does not undergo the corresponding dehydrogenation reaction to the fused 1,12-diazaperylene under identical conditions.

Having demonstrated the feasibility of the above approach, we were prompted to apply it to more complex systems where the synthesis of the free large-surface ligand is significantly more challenging.[8] Toward this end, Ru^{II} complexes of eilatin,[14] a marine alkaloid bearing two distinct coordinating faces (Scheme 3),[15] are particularly intriguing since they have recently been shown to exhibit anti-HIV activity.[16,17] The unfused ligand, trivially named here pre-eilatin, has been synthesized and used to prepare the dark-red Ru^{II} complex, $[Ru(bpy)_2(\text{pre-eilatin})]^{2+}$ (**3**).[10] Exposure to Pd/C in ethylene glycol at elevated temperatures (175–190 °C) cleanly converts complex **3** into the corresponding deep-green eilatin complex **4** after 1 h in essentially quantitative yield.[10] It is worth noting

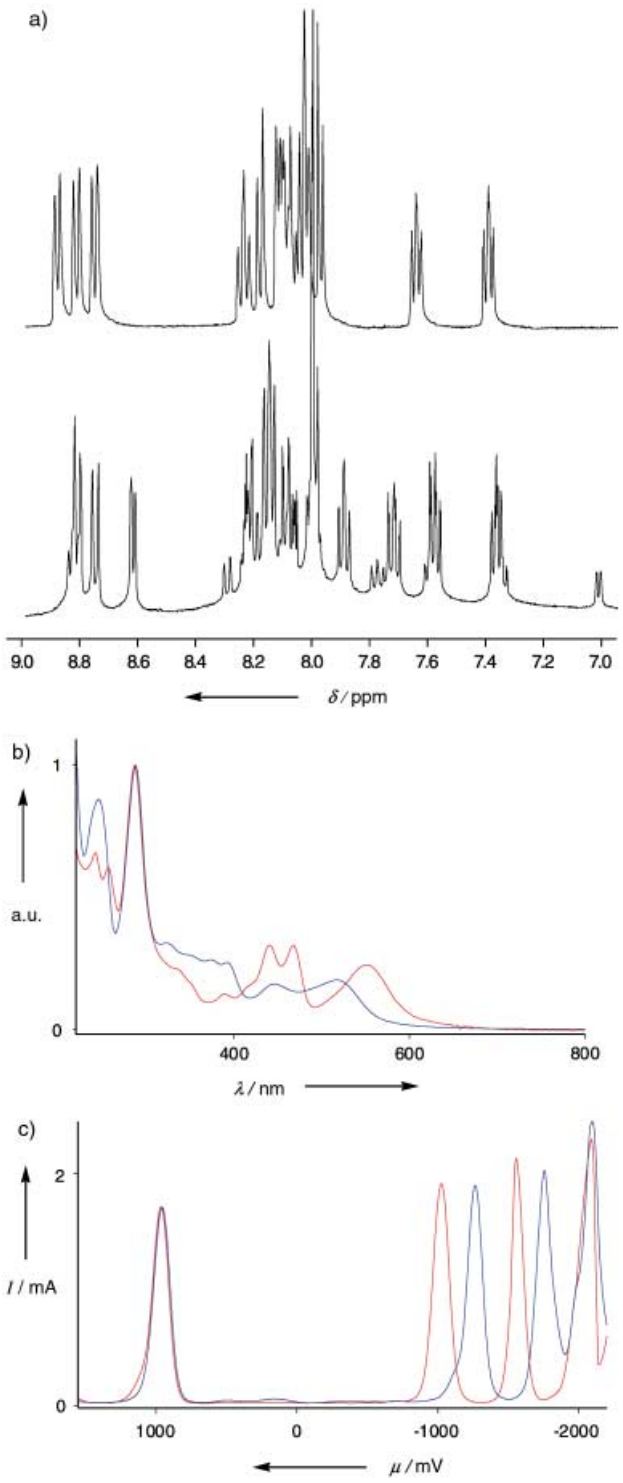


Figure 1. a) ^1H NMR spectra of **1** (bottom) and **2** (top) in $[D_6]$acetone at room temperature. b) UV/Vis spectra of **1** (blue) and **2** (red) in CH_3CN. c) Square-wave voltammograms of **1** (blue) and **2** (red) in CH_3CN containing 0.1 M $[nBu_4N][PF_6]$ as supporting electrolyte. Potentials are shown with reference to the ferrocene–ferrocenium couple at 0.08 V.[12]

that, as for the biisoquinoline system, treatment of the free pre-eilatin ligand with Pd/C under similar conditions does not yield eilatin (Scheme 3).

The structural and electronic reorganization that accompanies the transformation of **3** to **4** is manifested in a simplified NMR spectrum, a dramatic red-to-green color

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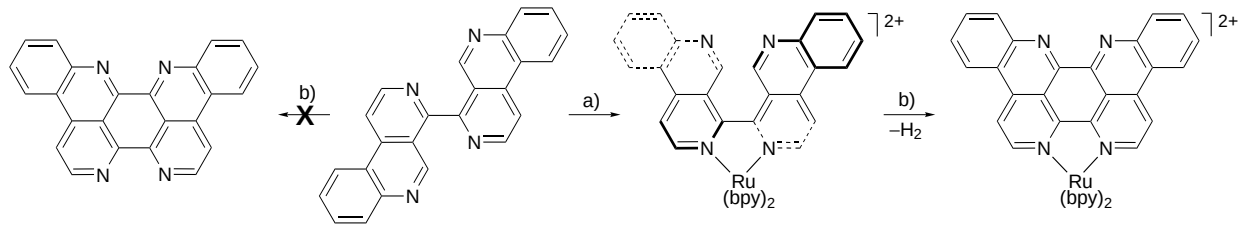


Eilatin Pre-Eilatin **3** **4**

Scheme 3. Dehydrogenation of $[Ru(bpy)_2(pre\text{-}eilatin)]^{2+}$ (**3**) to $[Ru(bpy)_2(eilatin)]^{2+}$ (**4**). Reagents and conditions: a) $[Ru(bpy)_2Cl_2]\cdot 5H_2O$, ethylene glycol–water 1:1, 100 °C, 3 h, 62 % yield; b) Pd/C, ethylene glycol–acetone 10:1, 175–190 °C, 1 h, 97 % yield. All complexes were isolated as their PF_6^- salts.[10] Note that identical reaction conditions do not convert the free pre-eilatin ligand to eilatin.

change (Figure 2), and a substantial change in electrochemical characteristics.[10] As anticipated, complex **4**, containing the large-surface eilatin ligand, exhibits electronic transitions at lower energy than the bpy-type complex **3**. Most notable is the appearance of a low-energy band around 580–600 nm that has

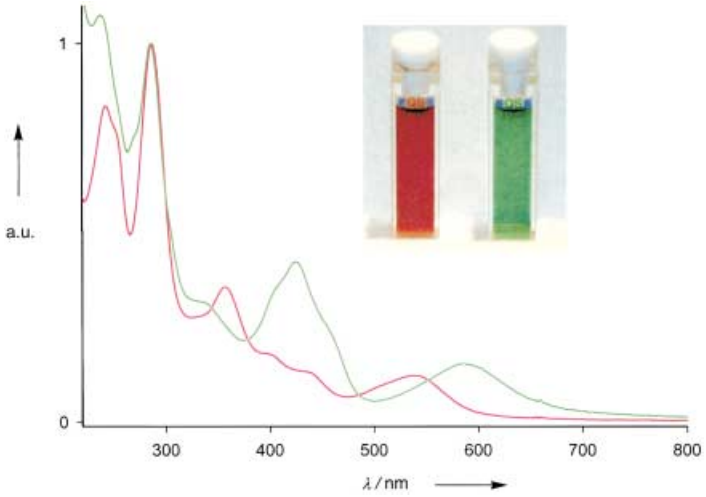
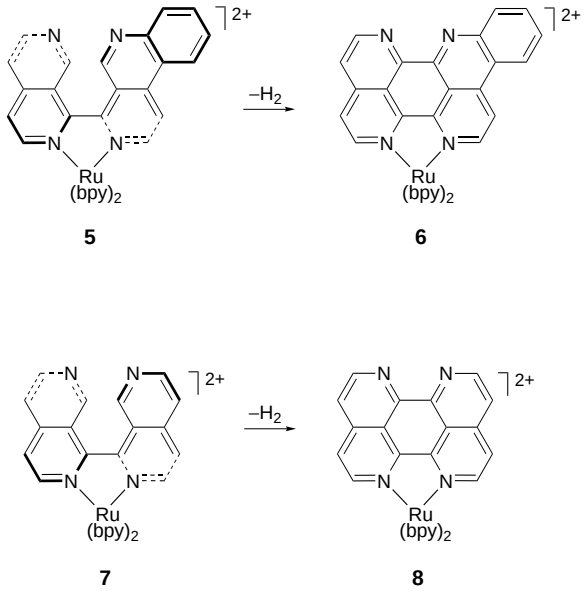


Figure 2. UV/Vis spectra of **3** (red) and **4** (green) in CH_3CN. Inset: a picture of the corresponding solutions.

previously been assigned to a Ru–eilatin MLCT transition (Figure 2).[14] Planarization of the large heterocyclic ligand also stabilizes the reduced states of **4** when compared to **3**. While the $E_{1/2}$ values for the $Ru^{3+/2+}$ couple in **3** and **4** are almost identical (1.38 and 1.40 V versus SCE, respectively), a significant shift to less negative potentials is apparent for the reduction waves, with the $E_{1/2}$ value for the first reduction couple changing by more than 0.3 V ($E_{1/2} = -0.70$ and -0.39 V versus SCE, for **3** and **4** respectively).[10,18]

The approach reported here naturally lends itself for the fabrication of coordination compounds bearing asymmetric "large-surface" ligands, since fluxional heterobiaryl ligands are accessible through cross-coupling reactions.[19] Such ligands are particularly attractive because of their potential photophysical as well as nucleic acid recognition properties.[4,20] As shown in Scheme 4, we have targeted the previously unknown debenzo-eilatin system **6**. Coordination of the free ligand to yield **5**, followed by dehydrogenation over Pd/C in ethylene glycol affords the desired compound **6**.[10,21,22]

Interestingly, the 1,6,7,12-tetraazaperylene core of eilatin has never been reported. This heterocycle is an attractive



5 **6**

7 **8**

Scheme 4. Dehydrogenation reactions of **5** and **7** to yield the novel complexes **6** and **8**, respectively. All complexes were isolated as their PF_6^- salts.[10]

bifacial bridging ligand that can be utilized for investigating charge-transfer phenomena in bimetallic complexes.[23] Complexation of 1,1′-bis-2,7-naphthyridine to $[Ru(bpy)_2]^{2+}$ to give **7** is followed by a facile dehydrogenation to afford the monometallic complex **8** (Scheme 4).[10,22,24] In the case of both complexes **5** and **7**, dehydrogenation to **6** and **8**, respectively, produces the same extraordinary color change as with the eilatin system. The successful synthesis of complexes **6** and **8** highlights the significant advantages presented by the new approach for the modular construction of coordination compounds that are currently inaccessible by traditional routes.

The results reported in this contribution illustrate an elegant methodology to novel metal complexes where the "classical" $[Ru(bpy)_2]^{2+}$ core is coordinated to unique large-surface ligands. The approach takes advantage of metal coordination to promote a dehydrogenation reaction, where extended bpy-type ligands are forced into a *syn* orientation within octahedral complexes. It is likely that the enforced proximity and enhanced steric repulsion within the bound ligand facilitates the single carbon–carbon bond-forming step during the dehydrogenation/cyclization reaction.[25] In addi-

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tion to the efficient synthesis of biologically active eilatin-containing complexes, Ru^{II} complexes of previously unknown ligands have also been prepared. It is anticipated that this methodology can be applied for the fabrication of other coordination compounds that contain different metal centers and coordination geometries.

Received: June 12, 2002
Revised: August 15, 2002 [Z19186]

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[8] While direct synthesis of large-surface ligands followed by metal coordination can provide an alternative scheme, the synthesis of sophisticated chelating heterocycles is often a multistep and low-yielding process.

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[10] See Supporting Information for additional experimental details.

[11] The atropisomerism of the 1,1′-biisoquinoline ligand gives rise to the diastereomeric $[\Delta/\Lambda\text{-}(\delta/\lambda\text{-}1,1'\text{-biiq})Ru(bpy)_2]$ complexes. See reference [9].

[12] Cyclic and square-wave voltammetry measurements were conducted in acetonitrile containing $[Bu_4N^+][PF_6^-]$ as supporting electrolyte.[10] Ferrocene and $[Ru(bpy)_3]^{2+}$ were measured as standards. Values were converted to the SCE scale assuming $E_{1/2} = 400$ mV for the ferrocene–ferrocenium couple, as suggested in N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877 – 910.

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[18] These are relatively low potentials for unsubstituted Ru^{II}–polypyridine complexes. For $[Ru(bpy)_3]^{2+}$ the first reduction wave $[Ru(bpy)_3]^{2+/+}$ takes place at -1.27 V versus SCE. Replacing bpy with a ligand containing electron-withdrawing groups leads to a substantial change in $E_{1/2}$. Thus, the redox couple $[Ru(5,5'\text{-biscarboxyethyl-bpy})_3]^{2+/+}$ appears at -0.66 V versus SCE. See: C. M. Elliott, E. J. Hershenhart, *J. Am. Chem. Soc.* **1982**, *104*, 7519 – 7526. The first reduction wave for $[Ru(dppz)_3]^{2+}$ has been reported at $E_{1/2} = -1.00$ V. See: M. N. Ackermann, L. V. Interrante, *Inorg. Chem.* **1984**, *23*, 3904 – 3911.

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[21] Since metal complexation and dehydrogenation both take place at elevated temperature in ethylene glycol, it is feasible to execute both steps as a "one-pot" transformation. Typical overall yields for the two-step transformation (that is, metal coordination followed by dehydrogenation) are approximately 50%.
[22] The removal of aromatic rings from the eilatin core, as in complexes **6** and **8**, results in higher susceptibility of the complexes toward oxidation. Products **6** and **8** have been isolated as a mixture of the Ru^{II} and Ru^{III} forms (see Supporting Information).
[23] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993–1019; V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759–833; F. R. Keene, *Coord. Chem. Rev.* **1997**, *166*, 121–159; M. D. Ward, F. Barigelletti, *Coord. Chem. Rev.* **2001**, *216–217*, 127–154.
[24] The overall yield for the two steps is 30%.
[25] It is likely that a thermodynamic impetus to redirect the "misdirected" metal–ligand bonds in the unfused precursors contributes to the driving force of these transformations. See ref. [9] for a discussion regarding the bonding in the fluxional unfused complex **1**.

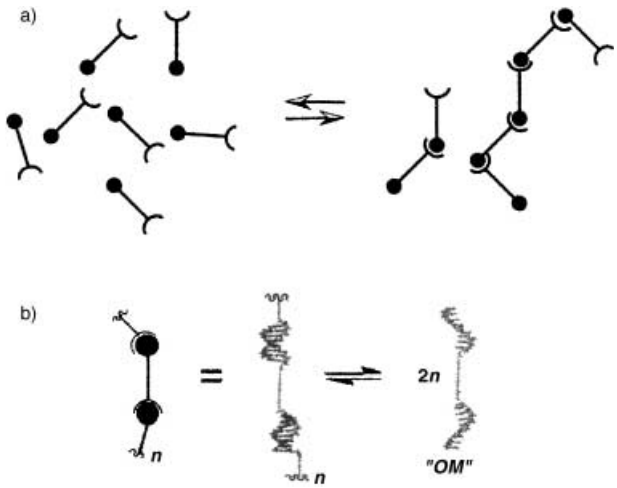

Figure 1. a) Schematic representation of reversible polymers; b) an OM-based reversible polymer. The spacer is extended for illustrative clarity only.

Modular, Well-Behaved Reversible Polymers from DNA-Based Monomers**

Elizabeth A. Fogleman, Wayne C. Yount, Jun Xu, and Stephen L. Craig*

Reversibly formed linear polymers (Figure 1a) have received increasing attention in recent years.[1–8] Reversible association of monomers leads to extended assemblies whose structure and properties depend on the strength and specificity of the association, the conformational flexibility of the molecule, the concentration of the monomer, and the chemical and physical environment of the system. These dissipative polymers undergo conformational changes and diffusion on much shorter timescales than their covalent counterparts, assemble with minimal imperfections, and repair themselves on useful timescales.[1,9] They encompass a range of structural motifs, phase behaviors,[1,3,10] solution and solid-state mechanical properties,[2,11,12] and environmental responsiveness,[12] and offer promise as environmentally benign materials as a result of the ease of processing and recycling and the absence of a polymerization catalyst. Meijer and co-workers[2,13,14] were the first to show that reversible polymers may possess properties that are similar to traditional covalent polymers despite the transient interaction (approximately seconds) defining the main chain.

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[**] This work was supported by the Petroleum Research Fund of the American Chemical Society and Duke University. Partial support was provided by the North Carolina Biotechnology Center and Research Corp. S.L.C. gratefully acknowledges a DuPont Young Professor Award and a Camille and Henry Dreyfus New Faculty Award.

Here we report that the reversible polymeric properties of a system based on oligonucleotide base pairing are well-behaved. The system is intrinsically modular and is therefore amenable to "physical organic chemistry of materials", that is, systematically varying the structure of the components and observing the concomitant changes in the properties of the assemblies. The monomers (hereafter, oligonucleotide-based monomers (OMs)) comprise oligonucleotide sequences that are covalently linked directly or through a synthetic spacer (Figure 1b). Duplex formation creates a linear, polymeric assembly that resembles larger duplex DNA,[15] but in which the main chain is defined by the reversible base pairing. The specificity between complementary DNA strands is such that monomers can be synthesized that associate head-to-tail or in alternating patterns. DNA base pairing is a popular motif for self-assembly,[16,17] and similar systems have been used to characterize DNA curvature and ring-closure probabilities,[18,19] to sequentially align synthetic moieties,[20,21] and to fabricate linear DNA–protein nanostructures.[22] Surprisingly, their properties in the context of reversible polymerization have not been previously reported. We find that OMs are well-suited to systematic studies of reversible polymerization.

Representative OMs are reported in Table 1. OMs **1a–d** are self-complementary and form single-component homopolymers, while **2A**:**2B** and **3A**:**3B** are two-component heteropolymer systems. Melting curves give effective free energies of dimerization[23] (ΔG_{dim}) that are in line with empirically derived expectations;[24,25] polymerization does not have a significant impact on duplex formation. Polymer formation is revealed in all cases by an increased viscosity in the OM solutions relative to solutions of nonpolymerizing analogues. For example, the viscosity of **2A**:**2B** (3 mg mL^{-1} or 0.29 mM in each monomer, 1M NaCl/10 mM sodium phosphate buffer, pH 7.0, 25.0 °C, Cannon–Ubbellohde viscometer) is 1.25 times that of the same concentration of **2B** alone, and that of **3A**:**3B** (5.8 mg mL^{-1} or 0.22 mM) is 2.5 times that of **3A** alone. The molecular weight of the polymer can be easily controlled by varying the ratios of **2A**:**2B** and **3A**:**3B**; an excess of any monomer serves as an effective "chain

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