Supporting Information

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Molecular Architecture towards Helical Double

Stranded Polymers

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Experimental procedures

Bis[4-(4-aza-tricyclo[5.2.1.0^{2,6}]dec-4-yl)-phenyl]methyl ferrocene-1,1'dicarboxylate **3.** To a solution of **5** (6.14 g, 22.4 mmol) in CH₂Cl₂ (90 mL) at 0 °C was added oxalyl chloride (3.9 mL, 44.8 mmol) and DMF (3 drops). The mixture was gradually warmed to rt and stirred for 3 h. The solvent was removed in vacuo to give the corresponding acid chloride which was used for the next reaction without further purification.

To a mixture of DMAP (5.48 g, 44.8 mmol) and **8** (10.91 g, 44.8 mmol) in THF (120 mL) was added the freshly prepared acid chloride described above in THF (120 mL). The mixture was stirred at rt for 3 h and a brownish solid was formed. CH₂Cl₂ was added and the solution was washed with water, brine (100 mL x 3) and then dried (MgSO₄). The solvent was removed in vacuo and the residue was recrystallized from CHCl₃/EA to get **3** as a light brown solid (10.80 g, 67%): mp 170-172 °C; IR: ν (cm⁻¹) 3060, 2954, 2866, 2837, 1704, 1615, 1525, 1475, 1368, 1277, 1191, 1134, 1024, 931, 803, 728; ¹H NMR (400 MHz, CDCl₃): δ 1.48 (d, *J* = 8.3 Hz, 2 H), 1.57 (d, *J* = 8.3 Hz, 2 H), 2.86 (dd, *J* = 9.5, 2.4 Hz, 4 H), 2.93 (bs, 4 H), 3.02-3.04 (m, 4 H), 3.17-3.22 (m, 4 H), 4.17 (s, 4 H), 4.72 (s, 4 H), 5.1 (s, 4 H), 6.09 (s, 4 H), 6.40 (d, *J* = 8.1 Hz, 4 H), 7.25 (d, *J* = 8.1 Hz, 4 H); ¹³C NMR (100 MHz, CD₂Cl₂): δ 45.5, 46.7, 50.6, 52.1, 66.6, 71.4, 72.9, 73.3, 111.6, 122.7, 130.1, 135.7, 147.8, 170.1; MS (FAB) *m/z* (rel intensity): 720.0 (M⁺, 0.5), 613.0 (10), 460.1 (8), 307.1 (30), 289.0 (20), 224.1 (15), 154.0 (100), 136.0 (63), 107.2 (20), 77.5 (14); HRMS (FAB). Calcd. C₄₄H₄₄FeN₂O₄: 720.2650; Found: 720.2658.

Polymer 4. Under argon atmosphere, a solution of (Cy₃P)₂Cl₂Ru=CHPh (16.4 mg, 0.02 mmol) in CH₂Cl₂ (2 mL) was added to **3** (144 mg, 0.2 mmol) in CH₂Cl₂ (8 mL). The mixture was stirred at rt for 80 min, quenched with ethyl vinyl ether (2 mL) and poured into EtOAc (25 mL). The solid was collected and washed with EtOAc and Et₂O to afford **4** as a brown solid (130 mg, 90%): IR: ν (cm⁻¹) 3050, 2929, 2830, 1707, 1615, 1523, 1464, 1368, 1274, 1185, 1129, 1029, 970, 803; ¹H NMR (400 MHz, CDCl₃): δ 1.20-1.90 (br, 4 H), 2.50-3.50 (br, 16 H), 3.95-4.45 (br, 4 H), 4.50-4.90 (br, 4

H), 4.90-5.70 (br, 8 H), 6.30-6.75 (br, 4 H), 7.10-7.50 (br, 4 H); ^{13}C NMR (125 MHz, CDCl_3): δ 36.0, 45.0, 46.6, 50.1, 66.5, 71.4, 73.0, 112.8, 123.9, 130.2, 131.4, 148.4, 170.4 (Peaks at 125.9, 128.4, 137.3 and 139.0 belong to the end groups of the polymer).

Methanolysis of 3. Under argon atmosphere, a mixture of **3** (0.2 g, 0.28 mmol) in CHCl_3 (20 mL), 10% aq NaOH (4 mL) and MeOH (10 mL) was stirred at rt for 20 h. CH_2Cl_2 was added. The organic layer was separated and washed with H_2O . The aqueous layer was acidified with conc. HCl and then extracted with EtOAc. The EtOAc layer was dried (MgSO_4) and the solvent was removed in vacuo to give **5** as an orange solid (76 mg, 99%). The organic layer was dried (MgSO_4) and the solvent was removed to afford **6** as a white solid (140 mg, 99%): mp 64-65 °C; IR: ν (cm^{-1}) 3038, 2962, 2841, 1615, 1566, 1522, 1477, 1367, 1345, 1256, 1184, 1089, 971, 904, 801, 743, 723, 632; ^1H NMR (400 MHz, CDCl_3): δ 1.52 (d, J = 8.2 Hz, 1 H), 1.61 (d, J = 8.2 Hz, 1 H), 2.89-2.92 (dd, J = 9.5, 2.7 Hz, 2 H), 2.98 (bs, 2 H), 3.06-3.09 (m, 2 H), 3.22-3.27 (m, 2 H), 3.33 (s, 3 H), 4.35 (s, 2 H), 6.16 (s, 2 H), 6.43 (d, J = 8.4 Hz, 4 H), 7.17 (d, J = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 45.5, 46.5, 50.6, 52.1, 57.3, 74.7, 111.7, 124.6, 129.4, 135.8, 147.4; MS (FAB) m/z (rel intensity): 255.1 (M^+ , 100), 224.1 (31), 188.1 (61), 158.1 (12), 144.1 (5); HRMS (FAB). Calcd. $\text{C}_{17}\text{H}_{21}\text{NO}$: 255.1623; Found: 255.1617; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}$: C, 79.96; H, 8.29; N, 5.49; Found: C, 80.01; H, 8.13; N, 5.32.

Methanolysis of 4. Under argon atmosphere, a mixture of **4** (0.08 g, 0.11 mmol) in CHCl_3 (8 mL), 10% aq NaOH (1.6 mL) and MeOH (4 mL) was stirred for 24 h at rt and worked up in a similar manner as described above to yield **5** as an orange solid (0.02 g, 66%). The organic solution was dried (MgSO_4) and evaporated in vacuo to give the residue which was dissolved in CHCl_3 . Methanol was added to precipitate polymer **7** as a grayish white solid (0.05 g, 89%): IR: ν (cm^{-1}) 3016, 2934, 2850, 1699, 1653, 1616, 1559, 1541, 1520, 1508, 1747, 1457, 1363, 1275, 1186, 1089, 970, 812; ^1H NMR (400 MHz): δ 1.20-1.50 (br, 1 H), 1.60-1.95 (br, 1 H), 2.50-2.80 (br, 2 H), 2.80-3.00 (br, 2 H), 3.00-3.50 (br, 7 H), 4.10-4.50 (br, 2 H),

5.30-5.70 (br, 2 H), 6.40-6.80 (br, 2 H), 7.05-7.25 (br, 2H). ^{13}C NMR (125 MHz): δ 36.0, 45.0, 46.4, 50.3, 57.5, 74.7, 113.0, 125.8, 129.4, 131.6, 148.3 (Peaks at 126.0, 128.5 belong to the end group of the polymer); The soluble portion showed GPC (THF): Mn, 7200; Mw, 10450; PDI, 1.45, corresponding to 28 repetitive units.

The integration ratio of the absorption due to the end group (vinylene group) at δ 4.90-5.20 and the olefinic protons at δ 5.30-5.70 was about 1 to 20 implying that **4** has 22 repetitive units.

Preparation of 9 from 7. Under argon atmosphere, a solution of **7** (255 mg, 1 mmol), and $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHPh}$ (82 mg, 0.1 mmol) in CH_2Cl_2 (47 mL). The mixture was stirred at rt for 2 h, quenched with ethyl vinyl ether (8 mL) and poured into MeOH (60 mL). The solid was collected and washed with MeOH to afford **9** as a grayish white solid (227 mg, 89%): IR: ν (cm^{-1}) 2940, 2857, 1620, 1522, 1478, 1362, 1189, 1093, 973, 910, 809, 753, 639, 522; ^1H NMR (500 MHz): d 1.35-1.55 (br, 1 H), 1.70-1.90 (br, 1H), 2.60-2.80 (br, 2 H), 2.80-2.98 (br, 2 H), 3.10-3.28 (br, 4 H), 3.28-3.40 (br, 3 H), 4.25-4.45 (br, 2 H), 5.30-5.60 (br, 2 H), 6.50-6.70 (br, 2 H), 7.10-7.20 (br, 2H); ^{13}C NMR (125 MHz): δ 36.0, 45.0, 45.2, 46.3, 50.3, 57.4, 74.7, 113.0, 125.8, 129.4, 131.5, 148.3 (Peaks at 126.0, 128.5 belong to the end group of the polymer); GPC (THF): Mn, 3535; Mw, 4538; PDI, 1.28.

2-Phenyl-4-styryl-6-vinyloctahydrocyclopenta[c]pyrrole 2. To a solution of 4-phenyl-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene (4.78 g, 20 mmol) and styrene (5.75 mL, 50 mmol) in dichloromethane (DCM, 250 mL) was added under argon $(\text{Cy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ (823 mg, 1 mmol) in DCM (20 mL). The mixture was stirred at rt for 24 h and then exposed to air for 30 min. The solvent was removed in vacuo and the residue was chromatographed on silica gel (hex/DCM = 1/1) to give **2** (5.15 g, 75%) as a white crystalline solid: mp 105-106 °C ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.60 (q, J = 12.8 Hz, 1 H), 2.07 (dt, J = 5.4, 12.8 Hz, 1 H); 2.95-3.20 (m, 2 H); 3.30-3.50 (m, 2 H), 5.14 (d, J = 10.4 Hz, 1 H), 5.18 (d, J = 16.8 Hz, 1 H), 6.10 (ddd, J = 7.2, 10.4, 16.8 Hz, 1 H); 6.40-6.52 (m, 2 H). 7.17-7.45 (m, 10 H); ^{13}C NMR (CDCl_3 , 100 MHz): d 36.4, 46.1, 46.5, 49.0, 49.8, 116.3, 126.7, 127.7, 128.5, 128.78, 128.81, 129.4, 131.2, 132.2,

136.6, 137.4, 175.9. IR (KBr) ν 3023, 2958, 2912, 2848, 1774, 1706, 1594, 1491, 1455, 1384, 1322, 1291, 1192, 1167, 107, 961, 921, 873, 815, 772, 755, 694, 622, 586 cm^{-1} ; MS (EI, 70 eV) m/z (rel. intensity) 343 (M^+ , 100), 314 (25), 252 (20), 239 (17), 196 (33), 175 (100), 165 (45), 141 (48), 128 (50), 115 (50), 105 (83), 91 (100). HRMS (EI) ($\text{C}_{23}\text{H}_{21}\text{NO}_2$): calcd: 343.1572; found: 343.1586; Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2$: C, 80.44; H, 6.16; N, 4.08; found: C, 80.62; H, 6.23; N, 4.41.

Electrochemistry Measurements. A potentiostat (EG&G 273A) with conventional three-electrode system [Pt disk (diameter = 3 mm) as the working electrode, Ag/Ag^+ as the reference electrode and Pt wire as the counter electrode] was employed for the cyclic voltammetry experiments using 0.2 M tetrabutylammonia hexafluorophosphate as the electrolyte. The system was purged with Ar for at least 10 min before experiments. Concentrations of monomer was 10^{-3} M in CH_2Cl_2 and the potentials are referenced to the redox potential of ferrocene/ferrocenium (Fc/Fc^+).

The cyclic voltammograms of **3** and **4** are shown in Figure 3. Two redox pairs with the formal potentials of 384 mV and 506 mV were observed for **3**, which corresponds to the redox process of the ferrocene and para-substituted aniline-like moieties, respectively. For polymer **4**, only one redox pair with the formal potential of 439 mV was observed. Presumably, the two redox pairs merged at the same potential in the polymer.

Figure 3. Cyclic voltammograms of (a) the 1st cycle of **3**, (b) the 1st cycle of **4** and (c) the 3rd cycle of **4**. The pre-peak (arrow) in the oxidative scan of **4** may be attributed to the adsorption of polymer onto the Pt electrode during the course of oxidation. This pre-peak disappeared in the third cycle and after.

Characterization by SPM (scanning probe microscopy). Measurements of TMAFM (Tapping Mode Atomic Force Microscopy) and STM (Scanning Tunneling Microscopy) were carried out with a NanoScope IIIa controller equipped with a Quadrex and a low current converter suitable for operation under conditions of high tunneling impedance (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA, USA). The typical bias voltage and tunneling current for STM imaging ranged from 0.15 to 1.5 V and from 10 to 300 pA, respectively. Commercially available cantilevers (non-contact silicon, NSC15/Pt/50, MikroMasch, Spain) and Pt/Ir tips (PT, Nanotips, Digital Instruments) were employed. The microscope was housed in a chamber where dry N₂ was purging throughout the experiments and the humidity was lower than 2%.

The deposition solution was 0.1-mM **4** in CHCl₃ or CH₂Cl₂ and did not contain salts or electrolytes. Samples for SPM characterization were prepared by placing a drop of the deposition solution on freshly cleaved HOPG (highly oriented pyrolytic graphite,

MikroMasch, Spain) with a Pasteur pipette. To remove trace amount of solvent, the sample was subjected to vacuum dry (~30 min, 120 mTorr) prior to imaging. The images were taken with the presence of both **4** and HOPG whose lattice spacing was used to calibrate the measurements.

TMAFM revealed that introducing one drop of **4** (0.1 mM) onto HOPG results in a jagged topography (Figure 4). The topographic feature of the vacuum-dry samples confirms the presence of **4** on substrate because the deposition solution had no salt content and the purity of the polymer was confirmed by spectroscopic means. To gain spatial resolution down to the molecular level, STM was employed for the subsequent study. In contrast to the rugged TMAFM images, STM generally shows features of Figure 1 on atomically flat HOPG substrate. Based on the difference in imaging mechanisms between TMAFM and STM, the discrepancy suggests that the STM tip penetrates into the polymer film. For samples prepared from diluted solutions (~ μM), the features of aggregates were rarely observed.

Figure 4. TMAFM image of a drop of **4** (0.1 mM) on HOPG. Imaging conditions: scan rate, 1.969 Hz; resonance frequency, 190 kHz.

Figure 6. (a) ^1H NMR and (b) ^{13}C NMR spectrum of **7a** from the hydrolysis of **4**.

(c) ^{13}C NMR spectrum of **7b** from ROMP of **6**.

(a)

Figure 7. Variable temperature ^1H NMR of **4** in CD_2Cl_2 .

Molecular mechanics and dynamics simulations

1. Method of calculation

Molecular mechanics and dynamics calculations^{S1-S3} were carried out to simulate the structures of monomer **3** and polymer **4** with different molecular weights using modified version of Universal Force Field^{S4-S6} as implemented in the molecular modeling programs (Accelrys Inc., San Diego, CA, USA). Force-field-based simulations use an explicit expression for the potential-energy surface of a molecule as a function of the atomic coordinates with a potential-energy expression as shown in equation 1.

$$E = \sum_b k^d (d - d^o)^2 + \sum_a k^q (C_o + C_1 \cos q + C_2 \cos 2q) + \sum_d k^f (1 - \cos n f) + \sum_w k^w [1 + \cos(n c - c_o)] + \sum_{ij} [(a_{ij} / r)^{12} - (b_{ij} / r_{ij})^6 + q_i q_j (1 / D r_{ij})]$$

The potential energy, E , is given by the sum of energy terms for bond lengths d , bond angles q , dihedral angles f , and inversion term (improper torsion angles due to out-of plane displacements), together with the van der Waals and electrostatic contributions. In this approach, we designed a simulation procedure as shown in the flow chart of Figure 8.

Step 1. Determination of the monomer structures and interactions between monomers

The stochastic conformational search method was employed to build up reasonable conformational ensembles. It involves systematic exploration of conformations by alteration of selected torsion angles in **3**. Monte Carlo method^{S2} was used in the random sampling procedure and the selection criterion was employed to either select or reject the change of the torsion angles in molecule. If the change in energy (ΔE) resulting from the move is negative, the move is selected. If (ΔE) is positive, the Boltzmann factor shown in Equation (2) is computed and a random number from 0 to 1 is generated.

$$F = \exp(-\Delta E / (RT)) \quad (2)$$

If the random number is greater than F , the move is selected. R is the Boltzmann gas constant and T is the absolute temperature in Kelvin. The search procedure followed by the energy minimization resulted in a set of acceptable structures consisting of monomer ensemble. Through the analysis of the energy distribution with conformations by considering intra- and intermolecular interactions, the nature of assembly of molecules can be derived.

Step 2. Determination of the stable conformation of the dimer

The flowchart shows the definition of the dihedral angles on the backbones of single stranded dimers and the definition of isotactic and syndiotactic stereochemistry. Through grid scan of the torsion angles ϕ_1 and ϕ_2 , the structures of dimers were constructed. Systems considering with and without pending groups were established and the favored dimer structures were obtained. These stable dimer structures were the basic unit to construct the 3-D topology of polymer **4**.

Step 3. Determination of the major conformations of single and double stranded polymer

Figure 9 reiterates how the polymer structures were established. The most important factors are the coupling between the torsion on backbone (ϕ_1 and ϕ_2) and the stacking of the pendent groups. Due to twisting along the z-axis, the bouncing stretching along z-axis, the tipping and inclining of pending group, the construction of doubled stranded polymers would be elaborated. By employing the results from the monomer and dimer ensembles obtained from steps 1 and 2, and according to the STM experimental data, enough information was obtained to program the operation for the construction of the crude structure of **4**.

The global geometry optimization of supramolecules is complicated^{S7,S8}. In this work several optimization methods were used to explore the potential energy surface of secondary structures of **4** more efficiently. Rigid body approximation algorithms S1-S3,^{S9} is especially useful in a complex supramolecule consisted of monomeric units. It treats whole molecules or subunits thereof as rigid units, which may reduce degrees of freedom throughout the minimization leading to faster convergence on the potential

energy surface. Furthermore, novel constraint and restraint methods^{S1} to modify the energy expression were incorporated within the global optimization procedure. Ensembles of single and double stranded polymers were calculated and their dynamic behaviors were investigated. From the statistic analysis of the trajectories, the major conformations of the double stranded polymer were compared with the STM images.

Figure 8. The flowchart of the simulation processes.

Figure 9 (a) Definition of the main inter-molecular torsion angles in backbone ϕ_1 and ϕ_2 . (Due to symmetrical structure, one half of the backbone is shown.) (b) Definition of syndiotactic and isotactic stereochemistry.

2. Results and Discussions

2.1 Conformation of monomer

The structure of **3** was optimized by molecular mechanics calculations. The optimization relied mainly on the variation of torsion angles shown in Figure 10a. The energy barrier for each of the torsion interconversion was low. The cyclopentadienyl moieties were found to rotate easily, influencing the spans of the monomer (end to end distance). As shown in Figure 10b, the carboxyl groups on the cyclopentadienyl moieties in **3** were located at the anti-position relative to the central ferrocene moiety, and this structure was used as a basis for estimating the secondary structure of double stranded polymer **4**.

Figure 10. (a) Torsion angles in **3** considered for the optimization of the structure. (b) Optimized structures of **3** in anti form.

2.1 Favorable stereochemical structures

2.1.1 Dimer without pendent group

Figure 11 shows the fully optimized structures of the dimers without the pendent group and compounds with trans double bond were more stable than those with cis double bond. The relative energy of the two conformational isomers in each dyad

(when the double bond was trans) was less than 1 kcal/mol, and the barrier for the interconversion was less than 2 kcal/mol.

Figure 11 The fully optimized conformations for the syndiotactic (syn and anti) and isotactic (syn and anti) dimers without pendent group.

2.1.2 Dimer having pendent group

In a manner similar to that described above, optimization of single stranded dimer having pendent group was carried out by changing the torsion angles shown in Figure 10 and the results are summarized in Table 1. However when pendent groups (benzene ring and ferrocene moiety, etc) were attached, the syn conformations were more stable by at least 10 kcal/mol than the anti isomers. Figure 12 shows the isotactic and syndiotactic dimer structures. The isotactic stereochemistry appeared to be more favored than the syndiotactic isomers. Presumably, the stacking of ferrocenes^{S10-S12} and π - π interactions^{S13} between benzene rings in the pendent groups may play an important role to dictate the stereochemistry of these dimers. Slight perturbation of the torsion angles ϕ_1 and ϕ_2 around the trans double bonds (Figure 12c) may affect interactions between neighboring benzene rings and/or ferrocene moieties.

Table 1. The fully optimized conformations for the syndiotactic (syn and anti) and isotactic (syn and anti) dimers with pendent group

	syndiotactic		Isotactic		note
energy ^a	syn	anti	syn	anti	
<E(bond)>	17	17	16	16	stretching energy
>					
<E(ang)>	190	190	188	188	bending energy
<E(tor)>	53	54	52	54	torsion energy
<E(inv)>	0	0	0	0	out of plane energy
<E(vdW)>	149	161	141	159	van der Waals energy
>					
<E(elec)>	-266	-264	-257	-251	Coulomb energy
<E(MM)>	145	161	139	165	Molecular mechanical energy

^a Average energies from 100 structures, in kcal/mol.

Figure 12. (a) The isotactic single stranded dimer structure. (b) The syndiotactic single stranded dimer structure. (c) The trans double bond in isotactic stereochemistry and the definition of the torsion angles (C1-C2-C3-C4: ϕ_1 ? C3-C4-C5-C6: ϕ_2) on backbone.

The closest Fe-Fe distance in single crystal ferrocenes is 5.5-5.9 Å depending of the substituent(s) on ferrocene (Figure 13)^{S12,S14}. Interestingly, this distance is somewhat comparable with those of these dimeric isotactic structures where the neighboring Fe-Fe distances would be around 5.5 Å.

The structural parameters of these dimers may provide useful information on the structures of polymers. Although the neighboring benzene rings may not be parallel to each other and the ferrocene moieties may not be completely eclipsed, a rough estimation of the distance would be highly desirable. Accordingly, a parallel model was used (Figure 14a) and R1 and R2 are the vertical and horizontal distances between two benzene rings, respectively. Figure 14b is the stacking of ferrocenes where d1 is the Fe-Fe distance, d2 is the projection distance along Z axis and d3 is the closest H-H distance between two cyclopentadienyl moieties. These parameters could be characteristic from different isotactic dimer structures.

Figure 13. The crystal packing of ferrocene in P21/a array^{S12}.

Figure 14. (a) Definition of the distances between neighboring benzene rings in **4** and related systems. (b) Definition of the distances between neighboring ferrocene moieties in **4** and related systems.

2.1.3 Single stranded polymer

The dimer structure obtained from the previous calculations was used as the building blocks for the construction of single stranded polymers. The nature of the linkage (including torsion angles $\phi1$ and $\phi2$) between the two dimeric moieties in these newly constructed polymers would be the same as that of the connecting bonds between two monomeric units which form the dimer. Therefore, the polymeric backbone would become homogeneously as far as stereochemistry is concerned. Indeed, the geometries of the polymers would be strongly correlated with torsion angle $\phi1$ and $\phi2$ on the backbone. Again, the syn conformations in both isotactic and syndiotactic stereochemistries in single stranded polymers of different molecular weights were considered. The crude structures thus obtained were subjected to molecular mechanical optimization and constant temperature (300K) molecular

dynamics (MD) calculations.

The orientation of the pendent groups was found closely related to the tacticity of the polymer. In the syndiotactic syn conformation, the pendent group may be poorly aligned. If another norbornene moiety is attached to the other end of the pendent group, polymerization leading to a double stranded polymer may not proceed satisfactorily. On the other hand, the pendent groups are arranged coherently in the isotactic syn form. Similar strategy may be applied to yield selectively a double stranded polymer. Accordingly, isotactic syn stereochemistry was used for the calculations of doubled stranded polymers described below.

2.1.4 Major secondary structures of double stranded polymer

Three major classes of secondary structures of the double stranded polymer were obtained: double-stranded helix (A'), supercoil (B') and ladder (C') as illustrated in Figure 15. The geometric characteristics of the secondary structures obtained from this simulation are in good agreement with STM images.

Figure 15. Three major double stranded polymers: the doubled stranded helix

A'; the supercoil **B'**; the ladder **C'**

The optimal double-stranded helix as shown in Figure 15 had a diameter of 2.2 nm with 12 monomeric units in a pitch (12_1 helix). The central axis consist of the ferrocene segment has the freedom of twisting and bending even inclining in order to find the most stable stacking of ferrocene and benzene moieties in space through the variation of the torsion angles in molecule. Each of the monomeric layers in this helical structure is essentially parallel to each other. Interestingly, the helical structure may exhibit major and minor grooves due to the slight twisting of central axis due to the stacking of ferrocene moieties.

The supercoil structures appeared to be more flexible and the number of monomeric units in each pitch depends on the diameters of the coil (Table 2). Figure 15 shows the supercoil structure **B'** with 25 monomeric units per pitch and the diameter was 3.1 nm that is consistent with the STM structure **B**. When the diameter of the supercoil structure is large, the stacking of ferrocenes is prone to that in the ladder structure. On the other hand, the supercoil structure is more like the helical structure when the diameter is small. In addition, Figure 16 shows the different double stranded dimeric portions extracted form the three major structures of polymers. The relevant parameters for these structures are shown in Table 2.

Table 2. Structural parameters of three major secondary structures **A'**, **B'** and **C'**

	ladder	helix	supercoil
Stereochemistry	Isotactic_syn	Isotactic_syn	Isotactic_syn
Chiral sense	/	Right-handed /Left-handed	Right-handed Left-handed
Rotation per monomer unit pair	/	12	
Mean number per turn	/	12	12 ~ 30
Mean propeller twist	0°	~ 25°	twist +bending
Vertical distance (R1)	~ 3.8 Å	~ 3.2 Å	~ 3.5Å ~ 3.7Å
Horizontal distance (R2)	~ 4.4 Å	~ 3.8 Å	~ 3.7Å ~ 4.3Å
Fe-Fe distance (d1)	~ 5.9 Å	~ 4.9 Å	~ 5.3 ~ 5.7 Å
Project distance to Z axis (d2)	~ 5.7 Å	~ 4.5 Å	~ 5.2 ~ 5.6 Å
Closest H-H distance (d3)	~ 2.5 Å	~ 2.1 Å	~ 2.2Å~ 2.3Å

Pitch per turn	/	~ 53 Å	~ 53 ~ 80Å
Diameter	~ 25Å	~ 22Å	~ 22Å ~ 33Å

Figure 16. The structures of two monomeric units in (a) helical, (b) supercoil, (c) ladder forms of the polymer.

2.2 Potential energy

The “gas phase” energies of the secondary structures (helix **A'**, supercoil **B'** and ladder **C'**) of 12 repetitive units (without solvent), divided into electrostatic, van der Waals, and internal (bond, angle, and dihedral) energies, are given in Table 3. The average energy for each form was obtained from 100 snapshots. As can be seen from Table 3, the energies thus obtained may provide a qualitative picture of the relative stabilities of these secondary structures. Accordingly, the total molecular mechanical energy (E_{MM}) suggests that the supercoil structure would be lower than those of the other two structures. Presumably, the π - π stacking of aromatic rings, the interactions between ferrocene moieties, other electrostatic and van der Waals interactions may be

responsible for the relative stabilities of these structures.

Table 3. Molecular mechanical energy of three major conformational structures

energy ^a	helix	Supercoil	ladder	note
<E(bond)>	173	193	191	stretching energy
<E(ang)>	2281	2228	2241	bending energy
<E(tor)>	939	673	685	torsion energy
<E(inv)>	17	11	10	out of plane energy
<E(vdW)>	1122	907	859	van der Waals energy
<E(elec)>	-3416	-2973	-2925	Coulomb energy
<E(MM)>	1115	1042	1065	Molecular mechanical energy

^a Average energies from 100 structures, in kcal/mol and each compared structure contains the same element number (12 monomeric units)

2.3 Transition between the major secondary structures

Figure 17 is a schematic map depicting the relation between these three major secondary structures on the potential energy surface. This energy surface was constructed based on the simulated gas phase energies of three local structures and transition energies of interconversions. The transition from A'-helix form to B'-supercoil form appeared to be particularly favorable. When the MD simulation started in the A' form within ~500 ps, the transition may occur in synchronized manners to reach the B' form. In a similar manner, A' form may also slowly relax to the C' form. As shown in Figure 18, the topology and relationship of these three structures can be more easily characterized by the linkage number $Lk^{S15,S16}$, a topological property which can determine the dimensional degree of double stranded configuration. The linkage number Lk is the sum of the twisting number (Tw) and the writhing number (Wr). Although the rigorous definitions of twist and writhe are complex, Tw is a measure of the helical winding of the double strands around each other i.e. the twist of monomeric units between each other; Wr is a measure of the

coiling of the axis of the double strand polymer i.e chiral bending or “writhing” of the central ferrocene groups. A right-handed coil is assigned a negative number (negative supercoiling) and vice versa. The partition of Lk between Tw and Wr is determined by energetics. In the ladder form, each monomeric unit (green) is parallel to others, neither twisting between monomers nor writhing (bending) would happen, so $Tw = 0$; $Wr = 0$ and $Lk = 0$. In the perfect double helix form, only twisting between monomeric units may take place and no writhing would occur, so $Tw = n$; $Wr = 0$ and $Lk = n$. The third possibility is, when $Tw = 0$; $Wr = n$ and $Lk = n$, a structure like roll-of-ribbon. The supercoil structure would have the topology between the helix and the ribbon-like structure.

Shear induced twist-writhe interconversion would be arisen from the coupling of the variation of torsion angles (mainly due to the ϕ_1 and ϕ_2) in the backbone. A slight variation in these angles may provoke a profound influence on the secondary structure.

Figure 17. Schematic map of the potential energy surface based on the simulated energies of three local structures A', B' and C' (each compared structure contains the same 12 monomeric units). The two axes, twisting number (Tw) and writhing number (Wr) define the geometrical characteristic of the topology of the secondary structures. The doubled stranded helix is in minima **A'**, the supercoil in minima **B'**, and the ladder in minima **C'**.

Figure 18. Definition of characteristic topology satisfying the basic relation $Lk = Tw + Wr$ ($Tw = Wr = 0$ for the latter form; $Tw = n$ and $Wr = 0$ for the helical form; and $Tw = 0$ and $Wr = n$ for the ribbon-like structure).

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