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Ladderphanes: A New Type of Duplex Polymers

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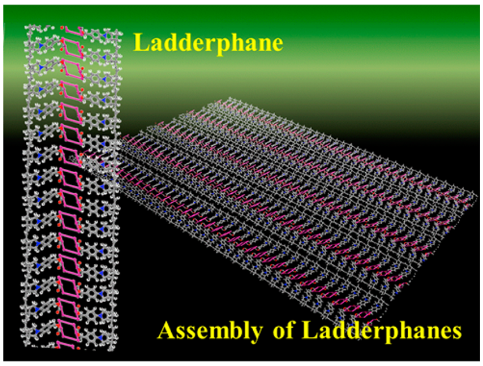

A polymeric ladderphane is a step-like structure comprising multiple layers of linkers covalently connected to two or more polymeric backbones. The linkers can be planar aromatic, macrocyclic metal complexes, or three-dimensional organic or organometallic moieties. Structurally, a DNA molecule is a special kind of ladderphane, where the cofacially aligned base-pair pendants are linked through hydrogen bonding. A greater understanding of this class of molecules could help researchers develop new synthetic molecules capable of a similar transfer of chemical information.

In this Account, we summarize our studies of the strategy, design, synthesis, characterization, replications, chemical and photophysical properties, and assembly of a range of double-stranded ladderphanes with many fascinating structures. We employed two norbornene moieties fused with *N*-arylpyrrolidine to connect covalently with a range of relatively rigid linkers. Ring opening metathesis polymerizations (ROMP) of these bis-norbornenes using the first-generation Grubbs ruthenium–benzylidene catalyst produced the corresponding symmetrical double-stranded ladderphanes. The *N*-arylpyrrolidene moiety in the linker controls the isotactic selectivity and the trans configuration for all double bonds in both single- and double-stranded polynorbornenes. The $\pi-\pi$ interactions between these aryl pendants may contribute to the high stereoselectivity in the ROMP of these substrates. We synthesized chiral helical ladderphanes by incorporating asymmetric center(s) in the linkers. Replication protocols and sequential polymerization of a monomer that includes two different polymerizable groups offer methods for producing unsymmetrical ladderphanes. These routes furnish template synthesis of daughter polymers with well-controlled chain lengths and polydispersities.

The linkers in these ladderphanes are well aligned in the center along the longitudinal axis of the polymer. Fluorescence quenching, excimer formation, or Soret band splitting experiments suggest that strong interactions take place between the linkers. The antiferromagnetism of the oxidized ferrocene-based ladderphanes further indicates strong coupling between linkers in these ladderphanes.

These polynorbornene-based ladderphanes can easily aggregate to form a two-dimensional, highly ordered array on the graphite surface with areas that can reach the submicrometer range. These morphological patterns result from interactions between vinyl and styryl end groups via $\pi-\pi$ stacking along the longitudinal axis of the polymer and van der Waals interaction between backbones of polymers. Such assembly orients planar arene moieties cofacially, and polynorbornene backbones insulate each linear array of arenes from the adjacent arrays.

Dihydroxylation converts the double bonds in polynorbornene backbones of ladderphanes into more hydrophilic polyols. Hydrogen bonding between these polyol molecules leads to self-assembly and produces structures with longitudinally staggered morphologies on the graphite surface.

1. Introduction

A polymeric ladderphane **1** is defined as a ladder-like polymer constituted of multiple layers of linkers tethered by two or more chains that are part of polymeric backbones.[1] Unlike most ladder polymers where two strands are directly connected by covalent bonds,[2−4] the linkers in ladderphanes are orthogonal to the polymeric strands and can be planar aromatic, macrocyclic metal complexes, or three-dimensional organic or organometallic moieties. They can also be considered as multiple layers of cyclophanes or, more precisely, a linear array of cofacially oriented arenes with polymeric backbones as the tethers. Therefore, the nature of the linkers plays an important role on the properties of ladderphanes. Within this context, a DNA molecule is

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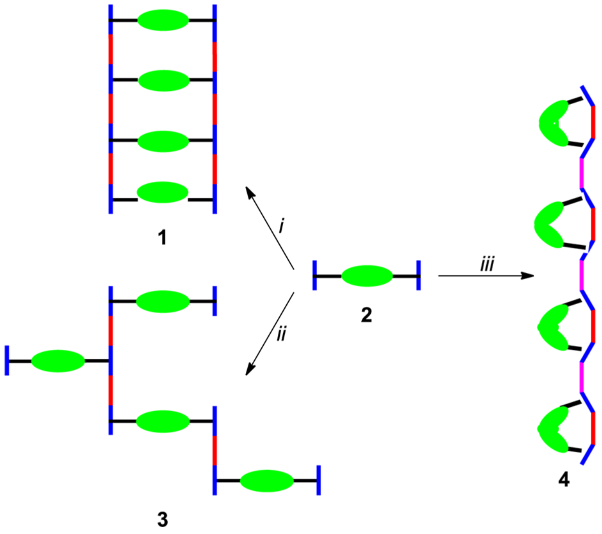
a special kind of double-stranded polymeric ladderphane where the base-pair pendants are connected through hydrogen bonding. The layers of base pairs in DNA, which are perpendicular to the polydeoxyribose-phosphate backbones, are cofacially aligned, and the spacing between these layers is 0.34 nm.[5] Thus, $\pi-\pi$ stacking between adjacent base pairs may play an important role, inter alia, for a DNA molecule holding the double helical structure,[6,7] and electron hopping between these layers has been explored.[8]

Cofacial long-range π-stacking toward highly ordered layer arrangement of aromatic rings could generate strong electronic coupling between these π-conjugated systems. Charge-carrier mobility would be closely related to such interactions.[9,10] Self-assembly of multichromophore building blocks for light harvesting and photophysical investigations has been explored.[11,12] Interactions between layered π-electron systems tethered by aromatic linkers[13] or oligophenylene[14] scaffold have been briefly examined. Large area processing with such cofacial alignment for device applications, however, is not trivial. Supramolecular architectures such as double-stranded ladderphanes **1** may offer an alternative entry to assemble these planar π-systems cofacially. In addition, the presence of polymeric backbones may serve as an insulator to isolate one array of such arenes from the adjacent arrays.

Besides directly covalently bonded ladder polymers,[2−4] double-stranded oligomers and polymers can be obtained by connecting two single-stranded oligomers or polymers via chelation to metal ions,[15,16] complexation through hydrogen bonding,[17−19] $\pi-\pi$ stacking,[20,21] ionic bonding,[22] or formation of double-stranded inclusion complex.[23] a double-stranded polysiloxane-based ladderphane using aromatic amides as linkers has been briefly explored.[24] Alternatively, two porphyrin-ethynylene polymeric chains are connected through dative bonds with 4,4′-bipyridine, which gives a ladderphane-like polymer.[25] It is worth noting that most of these synthetic double-stranded polymers have identical strands. Replication, in a sense, can be considered as using a single-stranded polymer template to build up a complementary daughter polymer via an unsymmetrical double-stranded ladderphane.[26] Artificial replication through complementary double helix formation has been briefly examined.[27,28] It is envisaged that, when the degree of polymerization and polydispersity of the template can be controlled, this protocol would furnish a new synthesis of daughter polymers with well-defined chain lengths and polydispersity.

SCHEME 1. Possible Polymerization Routes from **2** with Two Polymerizable Groups Linked by a Linker[a]



[a](i) Controlled polymerization; (ii) random polymerization; (iii) cyclopolymerization.

In this Account, we summarize our adventures on the strategy, design, synthesis, characterization, replication, chemical and photophysical properties, and aggregation behavior of double-stranded ladderphanes with fascinating structural varieties.

2. Strategy

The strategy toward a double-stranded polymeric ladderphane **1** relies on the design of a monomer **2** containing two polymerizable groups linked by an appropriate linker (Scheme 1). Branched random polymer **3** would be entropically favored, if no specially designed linker in **2** is employed (path ii). An alternative possibility would be a well-controlled reaction generating a double-stranded ladderphane **1** (path i). A rigid linker in **2** would be desired to avoid competitive intramolecular cyclization that may lead to a cyclopolymerization product **4** (path iii). It is envisaged that some kinds of interactions between linkers could possibly direct the orientation of the incoming monomer **2** during the course of the polymerization process. Several factors are indispensable to control the selectivity in this polymerization: (1) the nature of the polymerizable group, (2) the stereochemistry and conformation of the polymers, (3) the nature of the connecting group.

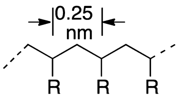
We have scrutinized the feasibilities of these features by a systematic study of single-stranded polymers that would allow us to understand the insights for the successful synthesis of double-stranded ladderphanes. Interactions between linkers via $\pi-\pi$ stacking during the course of polymerization might enable the reaction to proceed chemoselectively via path i (Scheme 1) giving ladderphanes. The following sections summarize how these strategies are executed for the successful construction of polymeric ladderphanes.

3. Choice of Polymeric Backbones

Polymers **5** derived from α-olefins would, however, not be suitable as the backbones for ladderphanes, because not only is the span by each of the monomeric unit (0.25 nm) far too short for $\pi-\pi$ interactions, but also the polymethylene skeleton would be conformationally too flexible. A more rigid backbone would therefore be desirable for this purpose.

Ring-opening metathesis polymerizations (ROMP) of norbornene derivatives under various conditions are well documented.[29−34] Polymers thus obtained are relatively rigid. It is envisaged that an appropriate choice of linkers to connect two norbornene moieties would enable selective synthesis of double-stranded ladderphanes.

3.1. Single-Stranded Polynorbornenes. Monomers **6** are easily accessible and the presence of the nitrogen atom in **6** offers a useful entry to symmetrically connect with a linker leading to a bis-norbornene-based monomer **7**. The incorporation of an *endo*-fused nitrogen heterocycle in **7** not only provides a more rigid framework for the polymeric backbones but also allows somewhat flexibility at nitrogen. Bisnorbornenes **7** [linker = $(CH_2)_n$] have briefly been employed as cross-linking agents for the ROMP with **6**.[34] In the presence of the first-generation Grubbs catalyst **8a**,[35] polymers obtained from **6**, in general, have atactic stereochemistry and contain a mixture of cis and trans double bonds.[33]



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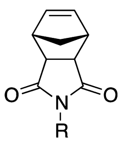

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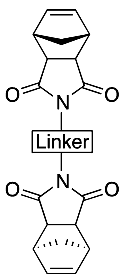

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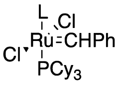
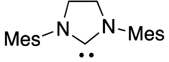
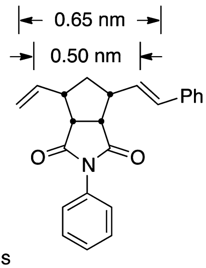


8a L = Cy_3P

8b L =





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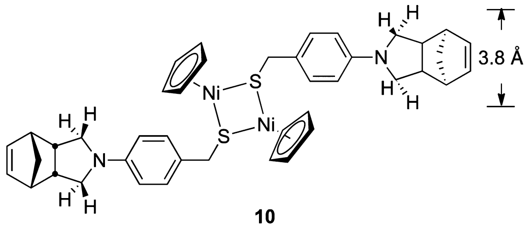
The repeat for each monomeric vinylcyclopentane moiety in polynorbornenes is around 0.5−0.6 nm as estimated by the X-ray structure of **9**.[36] Even though this spacing is somewhat larger than those for typical $\pi-\pi$ stacking between arenes, it offers a useful clue for the design of linkers in **1**. When the double-stranded nature of **1** is considered, the adjacent linkers are essentially parallel. The spacing occupied by the corresponding reduced pyrrolidine moieties as estimated by the X-ray structure of **10** would fit nicely into the linker.[37] Based on these considerations, bisnorbornenes fused with endopyrrolidine moiety **11** having different kinds of linkers are therefore chosen for monomer **2**.



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11

3.2. Stereochemistry of Polynorbornenes. The two norbornene moieties in **11** may not undergo ROMP at the same time. It seems likely that the pendants in a single-stranded polynorbornene should align essentially toward a similar direction so that the second strand could be formed accordingly. In addition, it is envisioned that a homogeneous tacticity of the two polymeric strands in **1** would be critical toward a successful synthesis of polymeric ladderphanes and the stereochemistry of double bonds in polynorbornenes should be well controlled.

The nature of the catalyst and the structure of norbornene substrates are known to determine the tacticity of the polymer and the stereochemistry of double bonds in polynorbornenes. Molybdenum-catalyzed ROMPs of norbornene derivatives give the corresponding polymers in cis and syndiotactic selectivity.[38,39] Similar reactions catalyzed by ruthenium-catalysts yield mainly trans-double bonds in polynorbornenes,[30,40] although predominant Z-selectivity was recently disclosed.[41] However, atactic polynorbornenes are generally obtained when ruthenium-based catalysts are used,[30,40,41] unless monomers are specially designed.[36,42−44] Indeed, ROMP of **12a** with **8a** gives exclusively trans-isotactic **13a**.[42,43] Diimide reduction of **13a** yields the reduced isotactic polymer **14a**.[39,43] Presumably, $\pi-\pi$ interaction between aryl pendants during the course of the polymerization process, inter alia,[45] may be one of the key factors for the

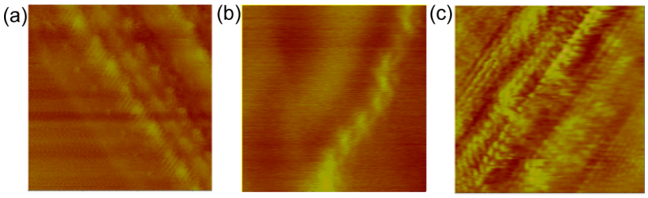
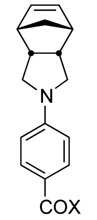
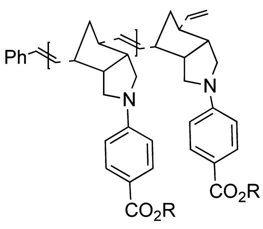


FIGURE 1. STM images of **27** on HOPG with (a) helical (16.8 nm × 16.8 nm), (b) supercoil (58 nm × 58 nm), and (c) ladder morphologies (7.2 nm × 7.2 nm).

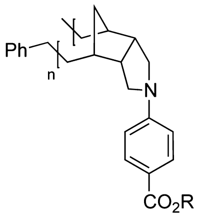
stereoselectivity of these reactions. Indeed, when the aryl pendant in **12** is replaced by a cyclohexyl group (as in **15**), polymer **16** contains 19% cis double bonds when **8a** is employed.[46] In addition, the stereoselectivity of ROMP of **12a** by the second-generation Grubbs catalyst **8b**[47] is not satisfactory.[46] Consequently, **8a** is used throughout this work.



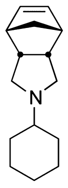
12a X = OEt
b X = OMe
c X = Cl



13a R = Et
b R = Me



14a R = Et
b R = Me



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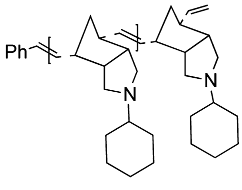

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3.3. Conformation of Aryl Pendants in Polynorbornenes. Second-order optical nonlinearity has been used to examine the conformation of polymers with dipolar pendants.[48] The enhancement of the second-order hyperpolarizability, β_o, values of **13b**[42] and related polynorbornenes **18**[36,43] in comparison with those of the corresponding monomers **12b** and **17** have been shown to be linearly dependent on the degree of polymerization. This observation suggests that the dipolar pendants in **18** may orient toward similar direction. The presence of double bonds in polymeric backbones in **13** or **18** governs the rigidity of the polymer, and the second-order nonlinear optical properties of the reduced analog **14b** rapidly reach saturation as the degree of polymerization increases.[42] In addition, the microscopic images of **19**[36] and **20**[46] offer a direct evidence for the rod-like structures.

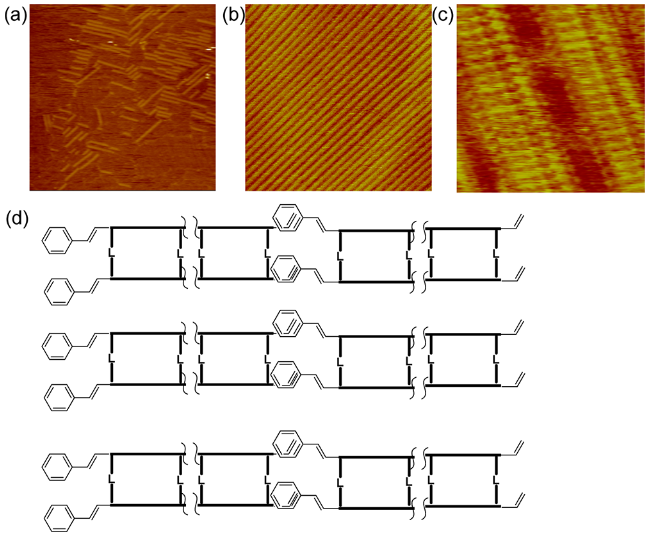
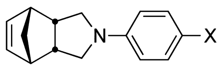


FIGURE 2. STM images of **31** on HOPG at (a) 100 nM (200 nm × 200 nm) and (b) 300 nM (100 nm × 100 nm) in phenyloctane. (c) High-resolution image of **31** (6.7 nm × 6.7 nm) on HOPG. (d) Diagram to illustrate the aggregation behavior of **31**.



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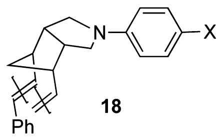

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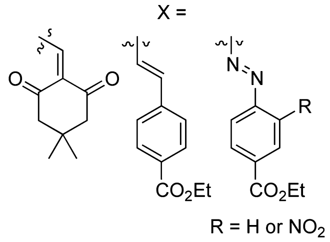

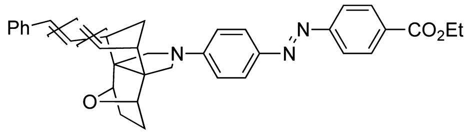

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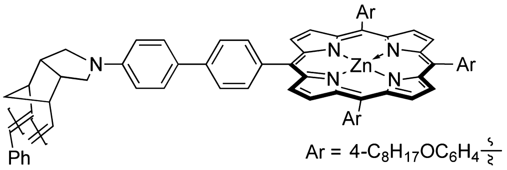

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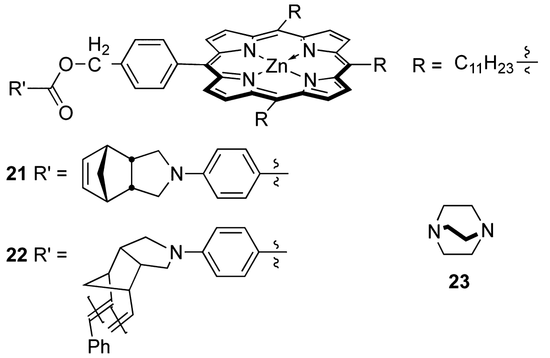
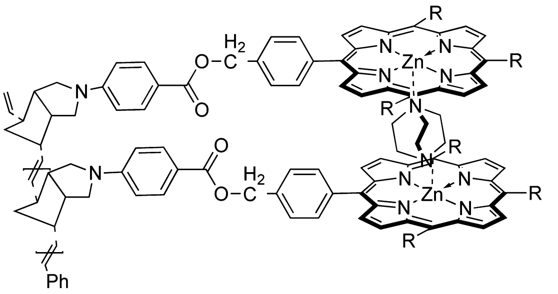
Other spectroscopic means are also consistent with the coherent alignment of pendants in these polynorbornenes. For examples, the chemical shifts of porphyrin protons in the ^1H NMR spectrum of **22** appear at higher field than those of the corresponding monomer **21**, and the exciton coupling between adjacent porphyrin pendants results in the Soret band splitting in the absorption spectrum of **22**.[46] In addition, bidentate DABCO **23** forms a complex with **22** to generate an array of porphyrin–DABCO (2:1) supramolecular scaffold **24**.[49] This evidence suggests that adjacent porphyrin moieties in these polymers are in close proximity.



21 R' =

22 R' =

23



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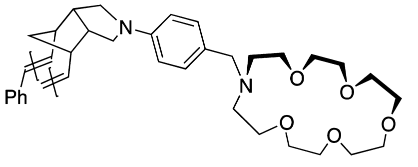
Polynorbornene **25** with monoaza-crown ether pendants becomes helical upon complexation with protonated amino acids as revealed by the enhancement of circular dichroic (CD) intensities.[50] Complexation of one crown ether moiety in **25** with the protonated ammonium ion and diastereoselective formation of hydrogen bonding between the carboxylic acid proton in the amino acid and the adjacent crown ether pendant may render unidirectional orientation of the pendants that would lead to a helical scaffold.



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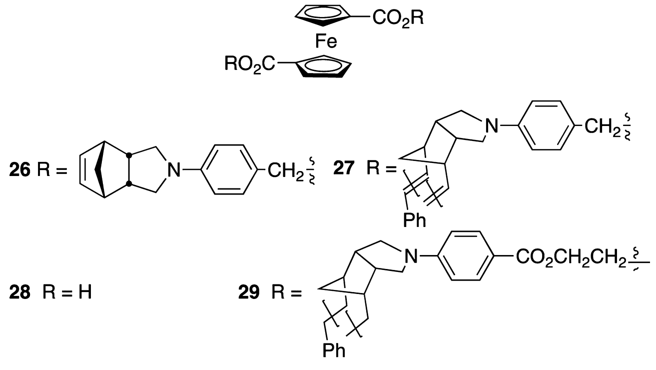
4. Linkers

As discussed above, norbornene fused with *endo*-*N*-arylpyrrolidine would be a promising building block for the construction of double-stranded ladderphanes, and the spacing occupied by each of the monomeric units in polynorbornenes is around 0.5−0.6 nm. The dimension of the linker should therefore be tailored within this range so that appropriate interactions between linkers might take place to direct the orientation of the incoming monomer during the course of the polymerization process. In addition, the linker should be relatively rigid but slightly flexible. Rigidity would be essential to correlate the orientation of two norbornene moieties for ROMPs leading to double-stranded ladderphanes. Since pendants in single-stranded polynorbornenes may not be arranged in eclipsed conformation, slight flexibility in the linker would also be necessary to bring the unreacted norbornene moiety on the pendants to the reaction center for the construction of the second strand in ladderphanes. Moreover, the linkers should be easily cleaved to furnish two single-stranded polymers. Thus, ester moieties are used to connect the linkers to the *N*-arylpyrrolidine-fused polynorbornene backbones. This strategy would be useful for structural elucidation of the double-stranded ladderphanes.

5. Symmetrical Double-Stranded Ladderphanes

5.1. With Ferrocene Linkers. A ferrocene linker is initially chosen because the X-ray structures of substituted ferrocene derivatives show that the Fe−Fe distances range from 0.55 to 0.59 nm, which would fit nicely into the space for each of the monomeric species in polynorbornene-based ladderphanes **1**.[51] In addition, the ferrocene moiety is not only rigid but also somewhat flexible.[52] Thus, ROMP of **26** catalyzed by **8a** affords double-stranded ladderphane **27**.[53] Alcoholysis of **27** gives ferrocene linker **28** and 2 equiv of single-stranded polynorbornene **30** with same degree of polymerization and polydispersity as that of **27**.[53,54]

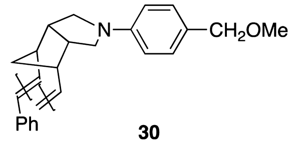


26 R =

27 R =

28 R = H

29 R =



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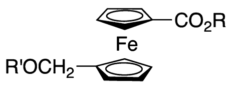

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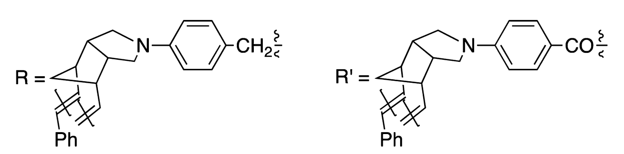


Scanning tunneling microscopic (STM) images of **27** on highly ordered pyrolytic graphite surface (HOPG), shown in Figure 1, indicate that double-stranded ladderphane **27** may

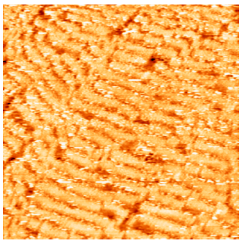


FIGURE 3. STM image of **29** on HOPG (45 nm × 45 nm).

adopt helical, supercoil, and ladder structures.[53] The average pitch length in the helical structure is 5.2 nm, which corresponds to 12 repeating monomeric units (Figure 1a). The 0.45 nm spacing between monomeric layers is somewhat shorter than the span for each monomeric vinylcyclopentane moiety described above, presumably due to helical morphology. Figure 1b shows the supercoil morphology that exhibits the average spacing per turn, apparent height, and nominal width of 7.1, 3.2, and 3.0 nm, respectively. The third type of image is the ladder structure with the width of 2.2 nm, and the spacing between the layers is about 0.5 nm, consistent with the structural feature of polynorbornene backbones (Figure 1c).

As can be seen from Figure 1, **27** may have a tendency to form aggregates. Indeed, related ladderphane **31**[55] forms a homogeneous two-dimensional ordered array on the HOPG surface at relatively higher concentration (>300 nM) in phenyloctane (Figure 2).[56] Although the average lengths of these polymers are 10–15 nm, the styrene and vinyl end groups in **31** may interact via $\pi-\pi$ stacking to form aggregates along the longitudinal axis of the polymer (Figure 2d). It is intriguing to note that the spacing between two terminal ferrocene linkers of adjacent ladderphanes, where $\pi-\pi$ interactions between the end groups may take place, appears to be similar to that occupied by each monomeric unit. When all double bonds on the polymeric backbones are reduced, such $\pi-\pi$ interactions between the end groups would no longer exist. Accordingly, breakpoints along the longitudinal axis of the hydrogenated polymer **29** are found in the STM image (Figure 3).[56] Side-by-side van der Waals interactions between the polymer chains, which will lead to aggregation in the second dimension, take place in both **29** and **31**.

As described in the following sections, STM images turn out to be a powerful arsenal to unambiguously determine the structures of polymeric ladderphanes. In addition, the well-assembled patterns on HOPG surface not only offer the structural information of these duplex polymers but also furnish a useful entry to assemble linker moieties coherently on graphite surface.

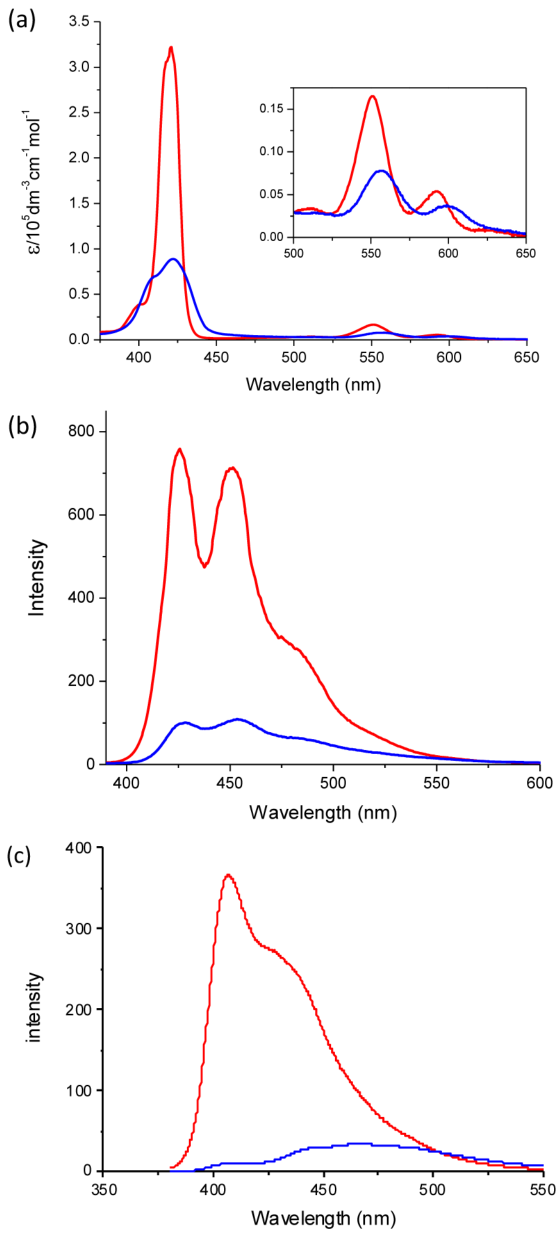
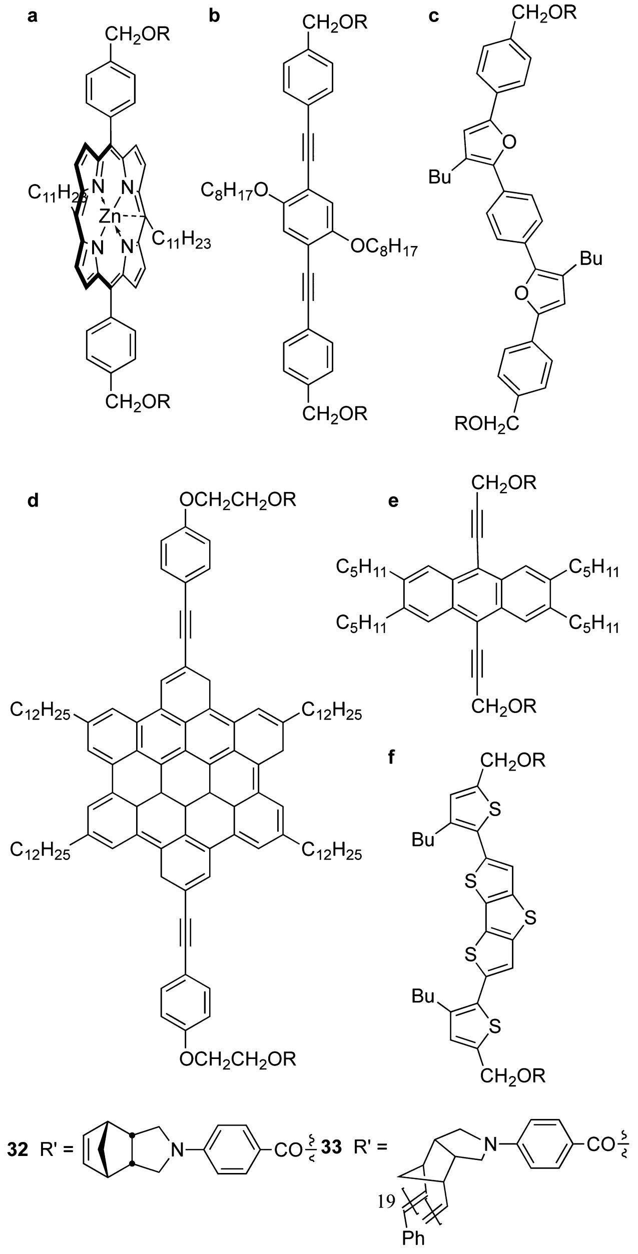


FIGURE 4. (a) Absorption spectra of **32a** (red) and **33a** (blue), (b) emission spectra of **32c** (red) and **33c** (blue), and (c) emission spectra of **32e** (red) and **33e** (blue).

5.2. With Aromatic Linkers. A range of different planar aromatic linkers have also been used for double-stranded ladderphanes **33**.[1,49,57,58] Photophysical studies suggest that there are significant interactions between the chromophores in these linkers. For examples, the Soret band splitting in the absorption spectrum of the polymer with porphyrin linker (**33a**, Figure 4a),[1,49] excimer emission with terphenylene–diethynylene linker (**33b**, Figure 4b),[1] and significant fluorescence quenching with oligoaryl linkers (**33c**–**f**, Figure 4c)[1,57] are characteristic photophysical properties of these polymers. In addition, the fluorescence lifetimes for **33c**–**f** are significantly reduced in comparison with those for the corresponding monomer **32c**–**f** and typical excimer lifetime for **33b** is observed.[1] It is known that interactions between two π-systems leading to perturbation of photophysical properties may depend on the distance and orientation between these two chromophores. When the distance is larger than 0.5 nm, the exciton coupling between these two chromophores would be relatively weak.[59] However, slight flexibility in the linker in **33** (benzylic or aliphatic moieties) might bring the adjacent chromophores to closer proximity to enable such interactions.



Triple-stranded ladderphanes **34** with multilayer planar oligoaryl linkers having C_3 symmetry are also prepared similarly.[60] Again, all linkers are cofacially aligned and interactions between these linkers lead to fluorescence quenching or perturbation of frontier orbitals resulting in shift of the emission maximum.

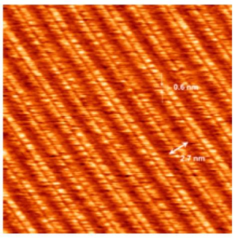
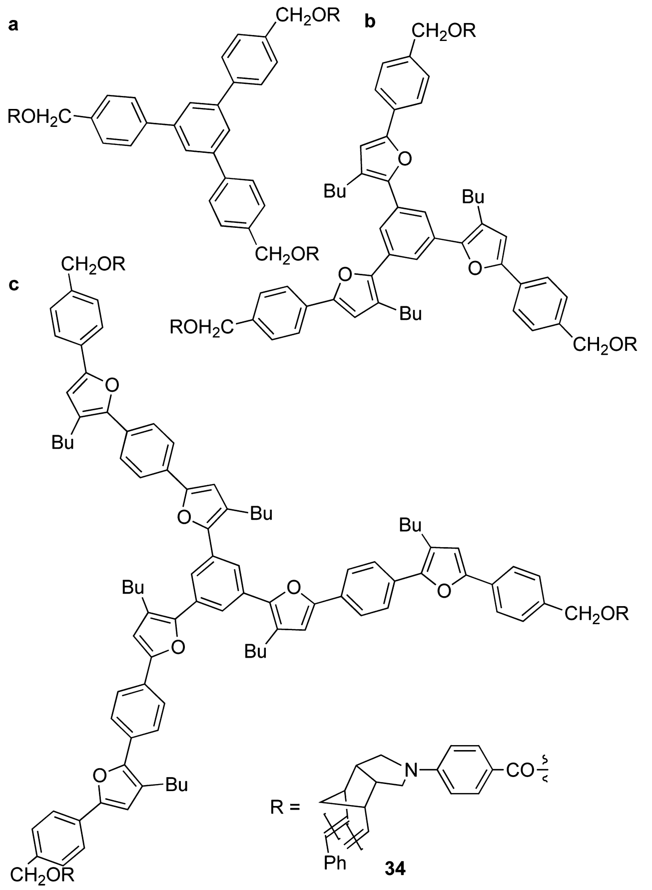
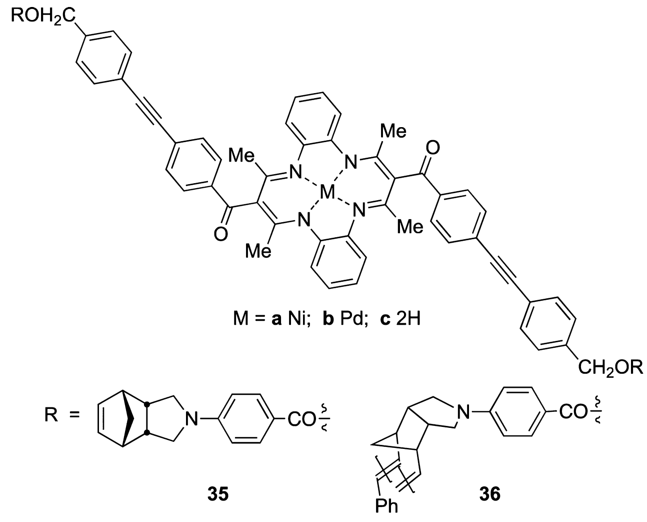


FIGURE 5. STM image of **38a** on HOPG (22 nm × 22 nm).



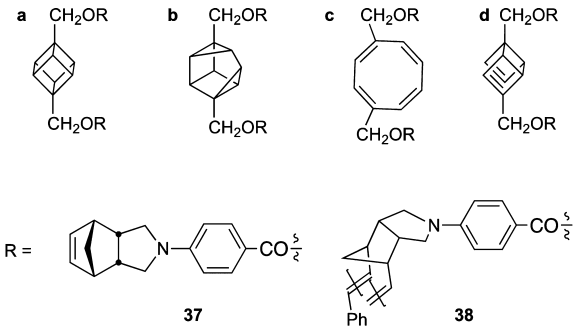
Similar to the STM images of ferrocene-linked ladderphane **31** (Figure 2), the films of ladderphanes **33** and **34** form an ordered two-dimensional assembly on the HOPG surface.[1,57,59]

5.3. With Antiaromatic Linkers. Double-stranded polymeric ladderphanes with 16-π-electron antiaromatic metallocycle linkers **36** are synthesized by the ROMP of the corresponding bisnorbornene monomers **35**. Unlike those with aromatic linkers described above, no changes in ^{1}H NMR, absorption spectra, and electrochemical oxidation potentials between these polymers and the corresponding monomers suggest that there would be no interactions between adjacent antiaromatic linkers in these polymeric ladderphanes.[61] The STM image of **36** is similar to those with aromatic linkers **33**.



35 **36**

5.4. With Alicyclic Linkers. Double-stranded ladderphanes having cubane (**38a**), cuneane (**38b**), and cyclooctatetraene (**38c**) linkers are synthesized by ROMP of the corresponding monomers **37**.[62] Surprisingly, tricyclooctadiene-linked polymer **38d** cannot be formed from the similar polymerization of **37d**, whereas cyclobutene derivatives are known to undergo ROMP upon treatment with a variety of metal−carbene catalysts.[63,64] Polymer **38d** is obtained by rhodium-catalyzed valence isomerization[65] of the cubane linkers in **38a**.



37 **38**

Similar to other ladderphanes, the STM image of **38a** shows a two-dimensional array. It is interesting to note that a dark line appears in the center along the longitudinal axis of the polymer separating each stripe into two symmetrical parts (Figure 5). Presumably, the nonconductive cubane moieties would align coherently along this dark line.

5.5. Helical Ladderphanes. Helical polymeric ladderphanes with C_2-chiral ferrocene linkers **40** are synthesized from the corresponding monomers **39**. As shown in Figure 6, the CD properties of **40** are significantly enhanced in comparison with those of the corresponding monomers **39** and the enantiomeric pairs of **40-*M*** and **40-*P*** exhibit mirror-imaged circular dichroic (CD) profiles.[66] The STM images of a single molecule of **40-*M*** and **40-*P*** indicate that they are helical and the aggregate form of **40-*M*** also exhibits zigzag morphology (Figure 7).

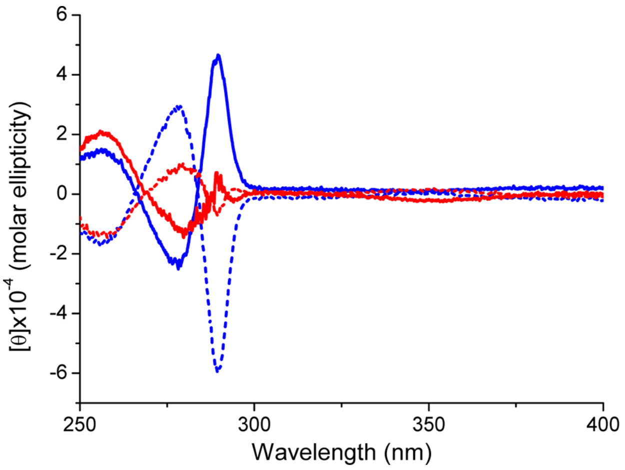


FIGURE 6. CD curves of **39a** (red dashed line), **40-*M*** (blue dashed line), **39b** (red solid line), and **40-*P*** (blue solid line) in DCM.

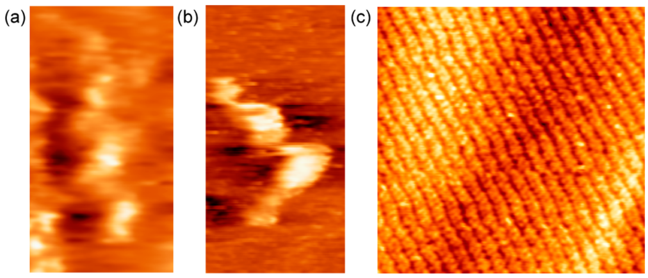
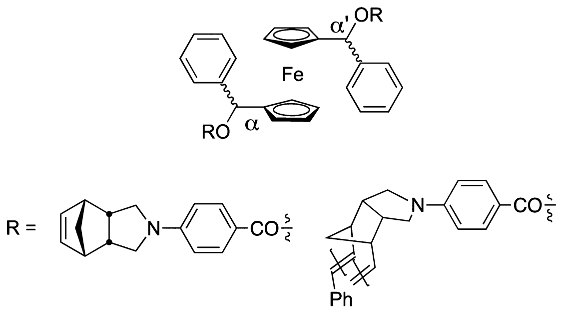


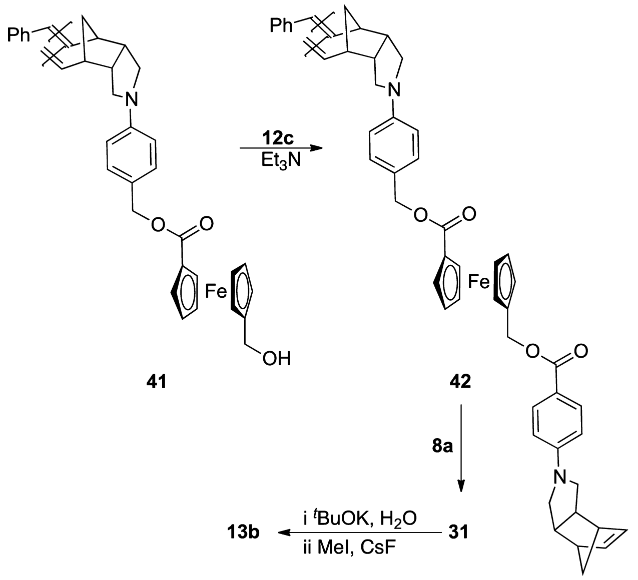
FIGURE 7. STM images of (a) **40-*M*** (10 nm × 20 nm), (b) **40-*P*** (10 nm × 20 nm), and (c) the aggregate of **40-*M*** (80 nm × 80 nm) on HOPG.



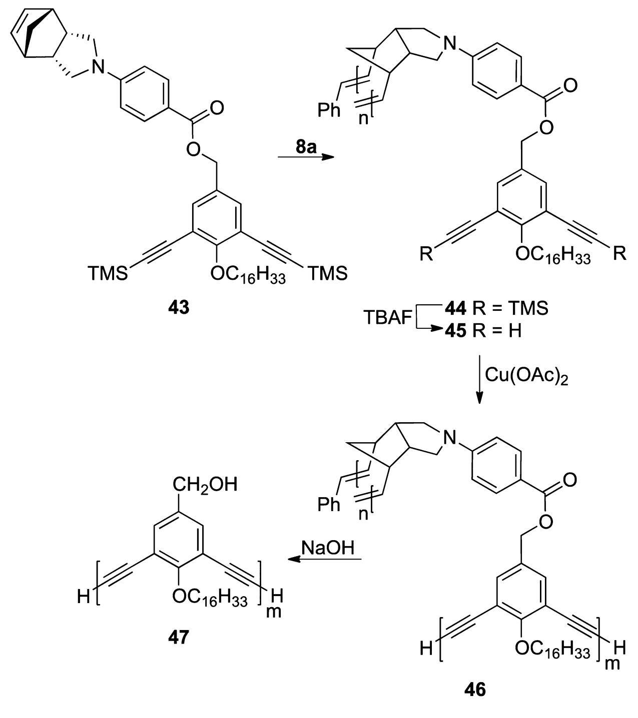
39a (*α*,*α*′ = *S*,*S*) **40-*M*** (*α*,*α*′ = *S*,*S*)
39b (*α*,*α*′ = *R*,*R*) **40-*P*** (*α*,*α*′ = *R*,*R*)

5.6. Thermal Stability of Ladderphanes. Polynorbornene-based ladderphanes described herein are quite thermally stable and the temperatures with 5% weight loss for **38**, for examples, are in the range of 240−300 °C as revealed by

SCHEME 2. Replication of **41** Giving Daughter Polymer **13b**



SCHEME 3. Sequential Polymerization of **43**

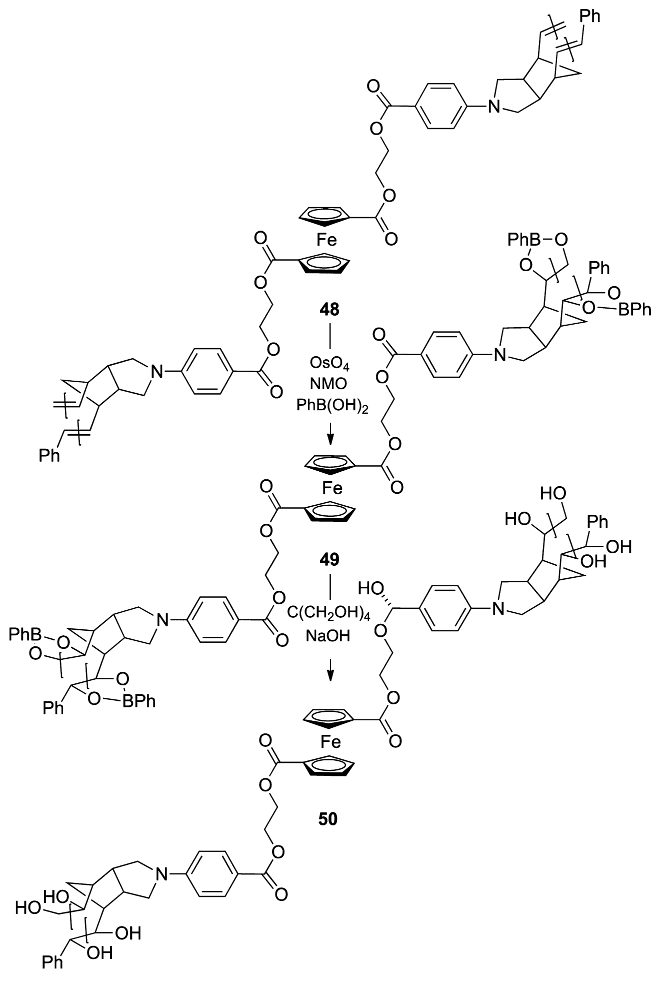


thermal gravimetric analyses.[62] Ferrocene-derived ladderphanes (e.g., **27**) behave similarly.[53]

6. Unsymmetrical Ladderphanes

6.1. Replication. One of the most important features of a DNA molecule is the ability to replicate. Scheme 2 summarizes the replication of **41** via covalent intermediates.[55] Thus, esterification of polyol **41** with **12c** gives **42**, which is treated with **8a** to yield the corresponding unsymmetrical ladderphane **31**. Upon hydrolysis followed by esterification, daughter polymer **13b** with the same number of repetitive units and polydispersity as those of **41** and **42** is obtained. Complexation with a polynorbornene template via hydrogen bonding has been used for the synthesis of a daughter polynorbornene[67] or a conjugated polymer.[68]

SCHEME 4. Dihydroxylation of **48**



6.2. Sequential Polymerization. Unsymmetrical double-stranded ladderphanes can also be obtained by sequential polymerizations of a monomer containing two different polymerizable groups. Monomer **43** contains a norbornene moiety, that can undergo ROMP to give a polynorbornene and two terminal alkyne groups, which can be transformed into a butadiyne by Glaser oxidation. Since ROMP of a cycloalkene catalyzed by **8a** is a living polymerization,[29] polymers **44** of different degrees of polymerization are obtained when different amounts of **8a** are used. In situ desilylation gives terminal alkyne intermediate **45**, which is oxidized with Cu(II) to afford the unsymmetrical polymeric

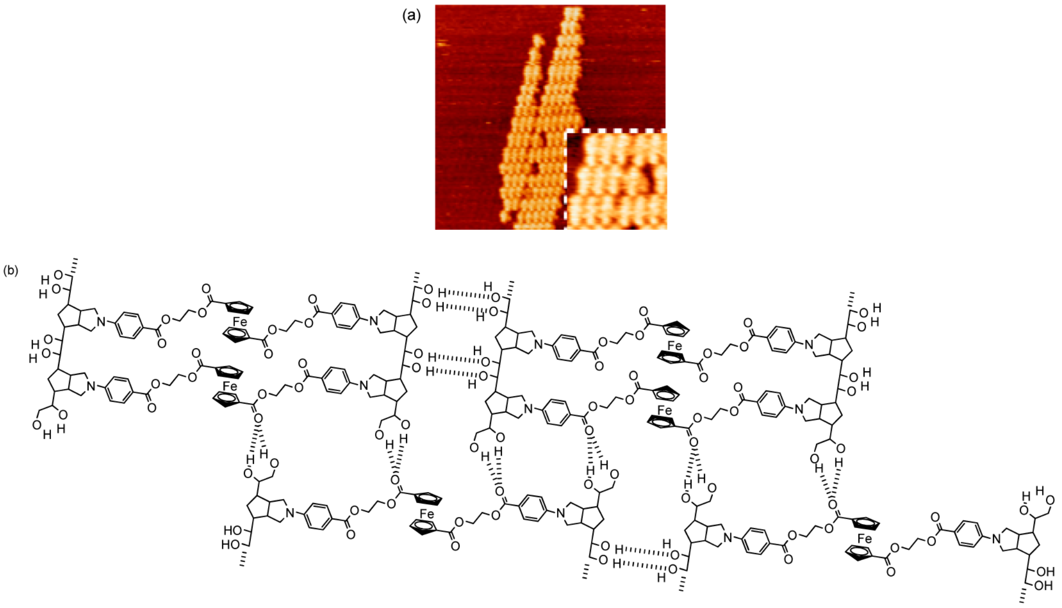


FIGURE 8. (a) STM image of **50** on HOPG (108 nm × 108 nm) and inset (24 nm × 24 nm). (b) Possible assembly of **50** by hydrogen bonding.

ladderphanes **46**. Base-promoted hydrolysis of **46** yields poly(arylene–butadiynylene) **47** (Scheme 3).[69] Like those of ladderphanes described above, the STM image of **46** exhibits well-aligned ordered morphology on HOPG with polynorbornene and poly(*m*-phenylene–butadiynylene) moieties in **46** assembled in an alternating manner.

7. Chemical Modifications of Ladderphane

7.1. Electrochemical Oxidation of Ferrocene Linkers. Ferrocene is redox active. Interestingly, about 70% of the ferrocenyl units in **40** and related polymers are oxidized by electrochemical methods.[70] The antiferromagnetic property of the oxidized **40** suggests that neighboring monomeric units in this oxidized **40** may strongly couple with each other so that the unpaired electrons in the oxidized **40** could be paired.

7.2. Dihydroxylation. The double bonds in **48** undergo dihydroxylation with OsO_4 under Narasaka conditions giving the corresponding polyboronate **49**, which is transesterified into **50** (Scheme 4).[71] The STM image of **50** on HOPG (Figure 8a) shows that polymers with equal lengths tend to align together, presumably due to full usage of all available hydroxyl groups on the polymeric backbones for hydrogen bonding. Unlike ladderphanes with vinyl and styrene end groups, adjacent molecules of **50** are assembled in staggered form along the longitudinal direction. It seems likely that hydrogen bonding may be formed between the terminal diols and the carbonyl groups in the ester linkers as illustrated in Figure 8b.[71]

8. Other Ladderphanes

Ladderphanes with skeletons other than polynorbornenes have recently been disclosed. Self-organizing, surface-initiated ring-opening exchange polymerization of cyclic disulfides furnishes ladderphane polymer on indium tin oxide surface as supramolecular n/p heterojunction architectures for double channel photosystems.[72–74] Polydiacetylene-based ladderphanes have recently been reported.[75]

9. Conclusions

This Account summarizes our recent studies on the double-stranded ladderphanes by means of ruthenium-catalyzed ROMP of bisnorbornene derivatives. The key to the success relies on the stereoselective formation of isotactic polynorbornenes with all double bonds in trans configurations. The presence of fused *N*-arylpyrrolidine moieties in the monomeric bis-norbornenes is essential to control the stereoselectivity of ROMP, presumably due to $\pi-\pi$ interactions between these pendants during the course of polymerization. Since linkers can be readily tuned, ladderphanes of different dimensions even with multiple strands can be facilely accessed. Although the spacing between adjacent linkers (0.45–0.55 nm) is somewhat larger than that expected for ordinary $\pi-\pi$ stacking, strong interactions between these linkers appear to take place.

One of the most important features of these ladderphanes is self-assembly to form large areas of two-dimensional highly ordered arrays. In this regard, all linkers are nicely aligned to submicrometer area. Such assembly furnishes an entry to orient planar arene moieties cofacially, while each linear array of such arenes is insulated from the adjacent arrays by polynorbornene backbones. The potential of using such assembled pattern in materials applications remains to be identified. Room for further research emanating from the present work abounds.

The replication protocol has been used to synthesize its complementary polymer via unsymmetrical ladderphanes. Polymers of well-defined chain lengths and polydispersity can be obtained. The ability to replicate a polymer would allow an alternative route for the transfer of information from one polymer into another via stable covalent duplex ladderphanes. The present status, however, is still far from similarity to a DNA molecule. Yet such a small step may pave the way for further elaboration toward better mimicking this important biomacromolecule.

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Tien-Yau Luh obtained his Ph.D. degree from the University of Chicago (with L. M. Stock) in 1974, did his postdoctoral research at the University of Minnesota (with P. G. Gassman), joined the faculty at the Chinese University of Hong Kong in 1976, and moved back in 1988 to his alma mater, National Taiwan University, where he is currently NTU Chair Professor. His current research interests include chemistry of materials and polymers.

FOOTNOTES

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The authors declare no competing financial interest.

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