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Polymeric Ladderphanes

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Abstract: A new class of polymers, which have a double-stranded polybinorbornene skeleton with multilayer planar oligoaryl linkers, defined as polymeric ladderphanes, are synthesized. The structures of these ladderphanes are determined by spectroscopic means. Photophysical studies and time-resolved fluorescence spectroscopic investigations reveal that there is a strong interaction between the chromophore linkers. Thus, Soret band splitting in the absorption spectrum of the polymer with porphyrin linker (**12e**), significant fluorescence quenching with oligoaryl linkers (**12b–d**), and excimer emission with a terphenylene-diethynylene linker (**12a**) are characteristic photophysical properties of these polymers. Scanning tunneling microscopy shows that polymers **12b** and **d** exhibit a ladder-like morphology and form a supramolecular assembly leading to a two-dimensional ordered array on a highly oriented pyrolytic graphite surface.

Introduction

A polymeric ladderphane is defined as multiple layers of cyclophanes^{1,2} where the tethers are part of the polymeric backbones (Figure 1a). Structurally, it can be considered as a multiple stranded polymer with planar aromatic linkers. A DNA molecule having a cofacial assembly of layers of base pairs can be regarded as a special kind of ladderphane, and electron hopping between these layers can readily take place.³ Indeed, interactions between two conjugated systems through face-to-face π – π stacking have played an important role for the extraordinary optoelectronic properties of aromatic compounds in the solid state as well as in solution.⁴ Cofacial arrangement of aromatic species (for example, pentacene)

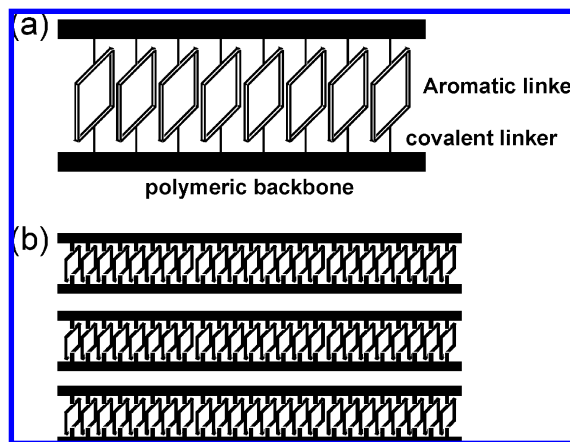


Figure 1. (a) Polymeric ladderphane; (b) assembly of ladderphanes to form a two-dimensional array.

appears to be critical to the performance of organic electronic devices.⁵ However, the orientation of conjugated molecules in the solid state would occasionally be difficult to control, and herringbone packing arrangement may, in general,

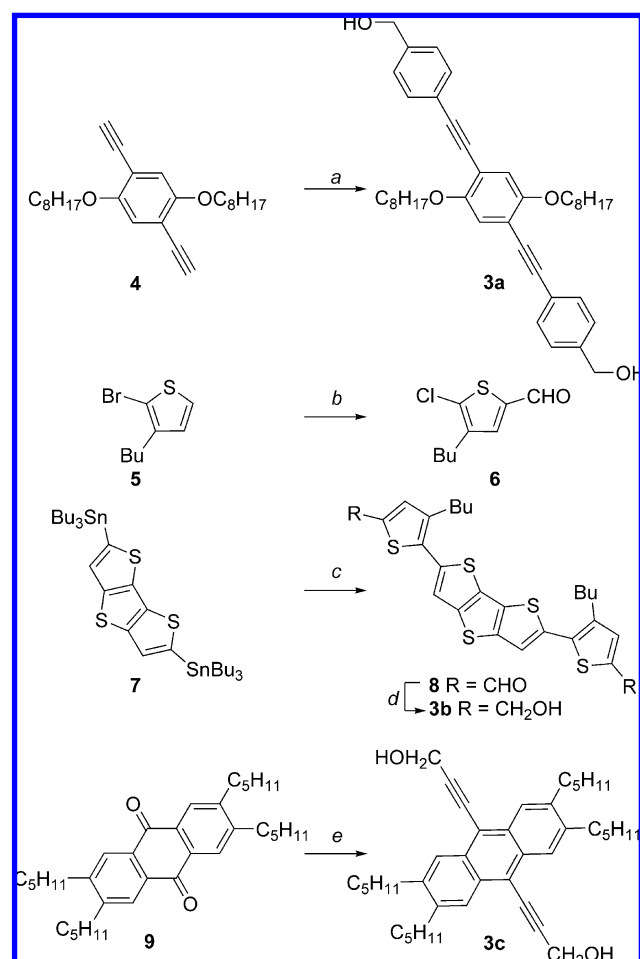
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Scheme 1^a

^a Reaction conditions: (a) 4-bromobenzyl alcohol, Pd(PPh₃)₄, CuI, ⁱPr₂NH, toluene, 80 °C, 84%; (b) POCl₃, DMF, 90 °C, 69%; (c) 6, Pd(PPh₃)₄, Cl₂, DMF, 100 °C, 43%; (d) NaBH₄, MeOH, THF, 0 °C, 94%; (e) (i) LiC≡CCH₂OTBS, (ii) SnCl₂·2H₂O/50%HOAc, (iii) TBAF, THF, rt, 39%.

constrict the charge mobility.⁶ Multilayered cyclophanes offered an interesting model for efficient transannular π -electronic interactions between aromatic rings.^{1,2} To the best of our knowledge, polymeric ladderphanes using planar aromatic moieties as linkers that are cofacially assembled in an array are unprecedented.

Table 1. Photophysical Properties of Monomers **11** and Polymers **12**

substrate	M_n (PDI)	λ_{\max}^a (nm)	λ_{em}^c (nm)	Φ_f^d	τ^f (ps)	λ_{em}^g
11a	1068	371 (31)	407, 428	0.82	1020	410–430
12a	46 000 (1.7)	371 (18)	407, 473	0.29	50 (22%), 1060 (78%), 830	380–400, 500–520
11b	1006	379 (25)	449, 476	0.30	552	450–470
12b	19 000 (1.68)	379 (22)	450, 480	0.10	80 (78%), 550 (22%)	450–470
11c	1040	445 (87)	459, 488, 520	0.70	12 400	450–470
12c	27 000 (1.72)	445 (29)	459, 488, 520	0.11	140 (44%), 12 400 (56%)	450–470
11d	1008	382 (53)	425, 451, 477	0.99	1080	440–460
12d	29 000 (1.74)	382 (37)	428, 454, 479	0.18	130 (50%), 1010 (50%)	440–470
11e	1304	421 (325)	598	0.04 ^e	1520	590–610
12e	31 000 (1.61)	422 (90)	608	0.01 ^e	160 (70%), 1520 (30%)	590–610

^a Absorption and fluorescence spectra were acquired at 10^{−5} M in CH₂Cl₂ (λ in nm). ^b Extinction coefficients (10³ M^{−1} cm^{−1}), based on the molecular weight of the monomeric unit. ^c Excitation at λ_{\max} . ^d The quantum yield was determined in CH₂Cl₂ (**a–d**) by employing coumarin-1 ($\Phi_f = 0.99$ in EtOAc) (ref 19) as the reference. ^e The quantum yield was determined in CH₂Cl₂ by employing ZnTPP ($\Phi_f = 0.033$ in toluene) (ref 20) as the reference. ^f Lifetime (ps) was measured in CH₂Cl₂. ^g Monitored wavelength in time-resolved fluorescence spectroscopy.

We recently reported that the ferrocene moieties in symmetrical or unsymmetrical double-stranded polybisenorbornenes **1** form a linear array with an Fe–Fe distance of ~ 5.5 Å, the spacing occupied by each of the monomeric units in these polymers.^{7–12} Because of such a short distance, the ferrocene moieties in **1** and related single- and double-stranded ferrocene appended polynorbornenes may interact strongly with each other as revealed by the electrochemical and magnetic studies.¹² We have established that ring-opening metathesis polymerizations (ROMPs) of the *endo-N*-aryl-pyrrolidine-fused norbornene derivatives catalyzed by Grubbs-I catalyst give the corresponding polynorbornenes in homogeneous tacticity with all double bonds in the trans configuration.^{7–12} Interactions between these pending aryl groups might take place during the course of the polymerization and would be responsible for the stereoselectivity of the polymerization reaction. Indeed, we have recently shown

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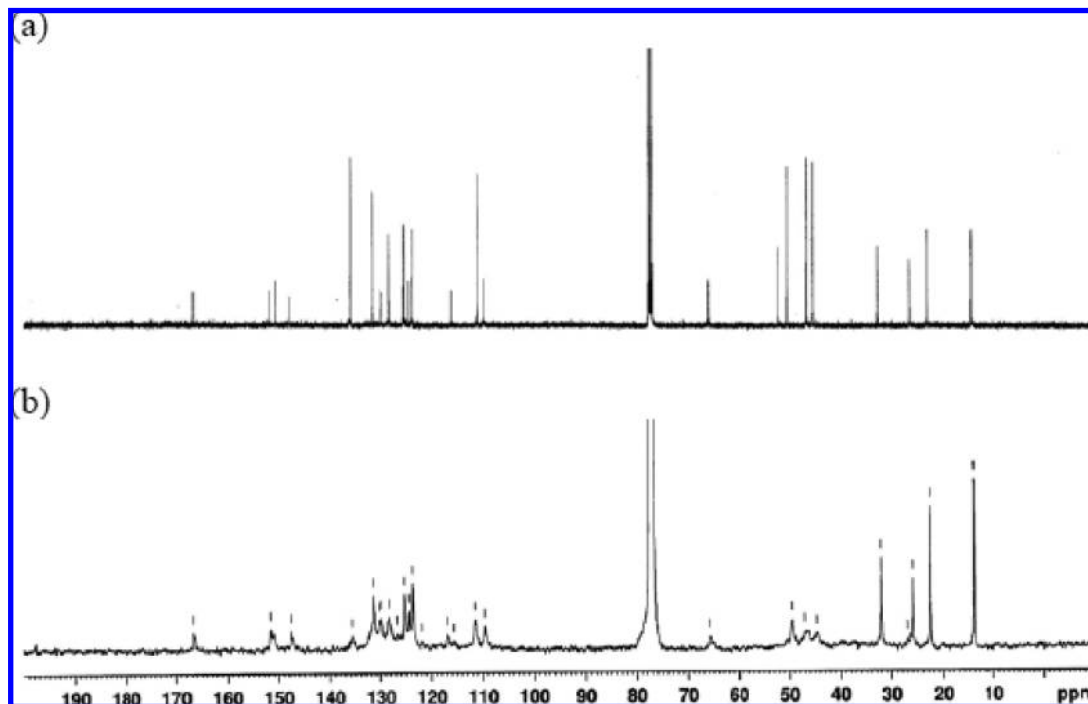
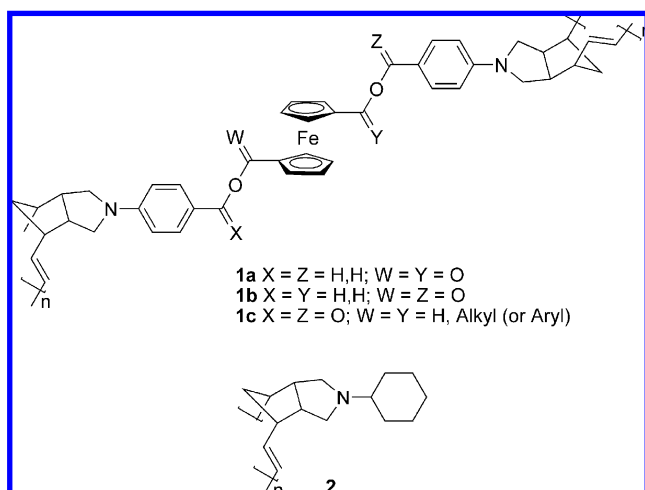


Figure 2. ^{13}C NMR spectra of (a) **11d** and (b) **12d**.

that a replacement of the endoaryl moiety by a cyclohexyl group (e.g., **2**) results in an atactic polynorbornene with a mixture of cis and trans double bonds.¹¹ In addition, several single-stranded polynorbornenes have recently been found to be useful for replication reactions to give the corresponding complimented polymers.^{9,13} This observation further indicates that all pending groups in these single-stranded polynorbornenes should be coherently aligned toward the same direction and the corresponding double-stranded polymers will be formed in these replication reactions.



Scanning tunneling microscopy (STM) investigations on double-stranded polymers **1** and related polybisenorbornenes indicate that these polymers can facily self-assemble to a submicrometer structure along the symmetric axes of highly

oriented pyrolytic graphite (HOPG) to form an ordered two-dimensional array.^{8,9} Presumably, π - π stacking among terminal groups in the longitudinal direction and van der Waal interactions between the polymeric backbones in the horizontal dimension may account for this highly oriented morphology. It is envisaged that the replacement of the ferrocene linker by an aromatic species would lead to a polymeric ladderphane that could serve as a molecular module to form a highly ordered two-dimensional aggregate, such as the one illustrated in Figure 1b, that could be considered as cofacial packing of aromatic moieties on a surface. We now wish to report the synthesis and properties of a series of polymeric ladderphanes based on double-stranded polybisenorbornenes using a range of different planar aromatic linkers.

Results and Discussion

The syntheses of aromatic linkers **3a–c** are summarized in Scheme 1, and the details are described in the Experimental Section in the Supporting Information. Linkers **3d**¹⁴ and **e**¹⁵ were obtained according to literature procedures. The incorporation of alkyl substituents in these linkers would increase the solubility of the corresponding polymers **12**. Esterification of **3** with **10a** under Mitsunobu conditions or with **10b** in the presence of Et_3N afforded the corresponding diesters **11**. ROMP of **11** using Grubbs-I catalyst¹⁶ yielded the corresponding polymeric ladderphanes **12**. The M_n values and polydispersities of **12** are summarized in Table 1.

Taking **12d** as an example, the chemical shifts in ^{13}C NMR spectrum were assigned based on ^{13}C - ^1H correlation spectra of **11d** and **12d** (Figures S13b and S24b). The ^{13}C NMR signal for the olefinic carbons shifted from δ 135.8 ppm in **11d** to δ 131.4 ppm in **12d** (Figure 2).¹⁷ The ^{13}C signals for each of the monomeric units in **12d** appear to be similar, if not identical. As can be seen from Figure 2, the ^{13}C NMR chemical shifts of **12d** matched nicely with those of **11d**.

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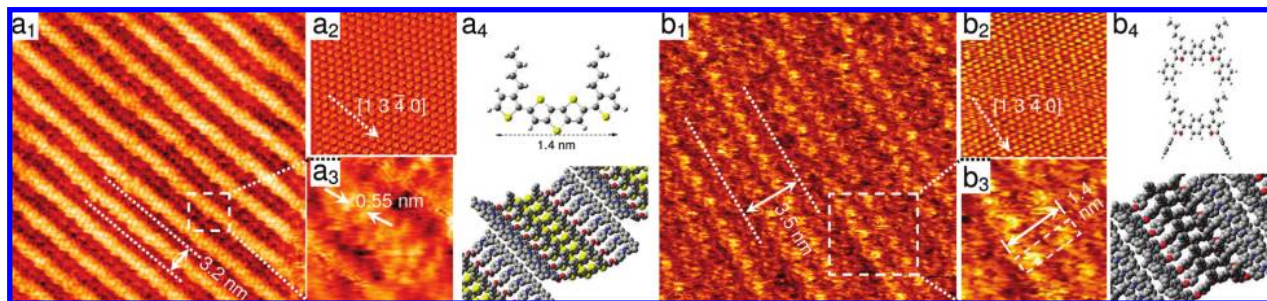
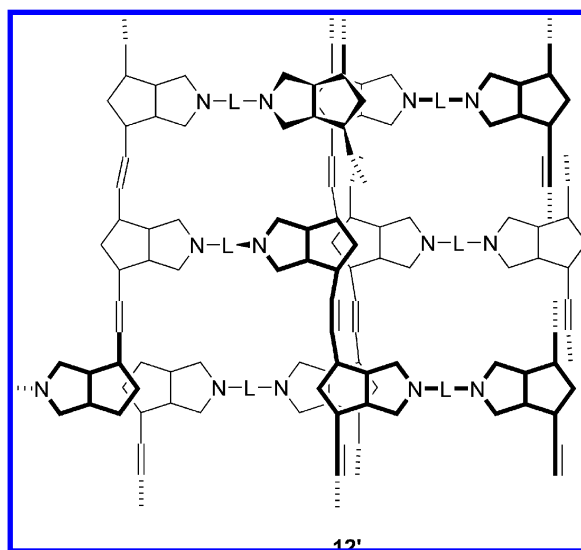


Figure 3. STM images of (a) **12b** and (b) **12d** on HOPG. Panels **a**₂ and **b**₂ were acquired by using an impedance smaller than that of panels **a**₁ and **b**₁ to unveil the underlying HOPG. Imaging conditions of E_{bias} , $i_{\text{tunneling}}$, and image sizes: (**a**₁) 0.90 V, 40 pA, 45 × 45 nm²; (**a**₂) 0.10 V, 0.20 nA, 4 × 4 nm²; (**a**₃) 0.90 V, 30 pA, 4 × 4 nm²; (**b**₁) 0.50 V, 10 pA, 15 × 15 nm²; (**b**₂) 0.10 V, 0.20 nA, 4 × 4 nm²; (**b**₃) 0.50 V, 10 pA, 4 × 4 nm².

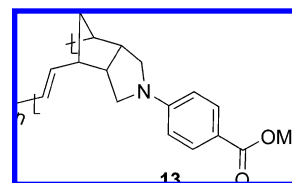
In general, the cis olefinic protons of polynorbornene appeared at higher field than those of the trans alkenyl protons in the ¹H NMR spectra.^{11,18} When polymers contain both cis and trans double bonds, two signals are commonly observed (e.g., **2**).^{11,18} It is noteworthy that a symmetric broad peak was observed for the olefinic protons of **12a–d** in ¹H NMR spectra. This observation may imply that the double bonds in these polymers would have the same configuration.

As can be seen from the ¹H and ¹³C NMR spectra of **12** (Figures S17–S26), no residual olefinic proton and carbon signals due to the unreacted norbornene moiety were observed. These results indicate that all norbornene moieties may have undergone an ROMP reaction under the polymerization conditions. If there was any branching in **12** (such as **12'**), the polymers would be expected to have a globular-like three-dimensional structure, which was not consistent with STM (scanning tunneling microscopy) results as described later.



Methanolysis of **12d** with NaOMe afforded the corresponding single-stranded isotactic **13** ($M_n = 6800$, PDI = 1.1) and linker **3d** in 83% and 85% yield, respectively. Moreover, all double bonds in **13** were in the trans configuration.^{10a,b} The narrow dispersity of **13** and similar degree of polymerization of **13** (25 monomeric units) and **12d** (28 monomeric units) suggest that the polynorbornene moieties in **12d** should have a chain length similar to that of **13**. These results provided additional evidence for the double-stranded structure of **12d** and solid support for the stereo-

selective ROMP of bisnorbornenes **11** leading to double-stranded polymers **12**. Again, the branched structure for **12** could be ruled out.



STM Imaging. Figure 3 shows STM images of **12b** and **d** dropcast on HOPG. Similar to the case for ferrocene-linked double-stranded polybisnorbornenes, the films of **12b** and **d** formed an ordered two-dimensional assembly on HOPG due to π – π attractions between end groups (vinyl and styryl) along the longitudinal axis and van der Waals interactions between the neighboring polymeric backbones along the second dimension.^{8,9} For the assemblies of **12b** and **d**, the nominal widths of these polymers were ca. 3.2 and 3.5 nm, respectively, which correlated quite well with the widths of the corresponding monomeric units. The spacing between each of the linkers in **12b** and **d** was ~0.5 nm which was the typical spacing occupied by each of the monomeric units.^{10a} The bright features of the STM images were attributed to the oligoaryl linkers of thiophene-containing **12b** and benzene-furan pentaaryl **12d**. The distance between the tips of the two terminal thiophene rings in the linkers of **12b** would be ~1.4 nm²¹ which was consistent with the width of the bright feature of the STM image of **12b**.

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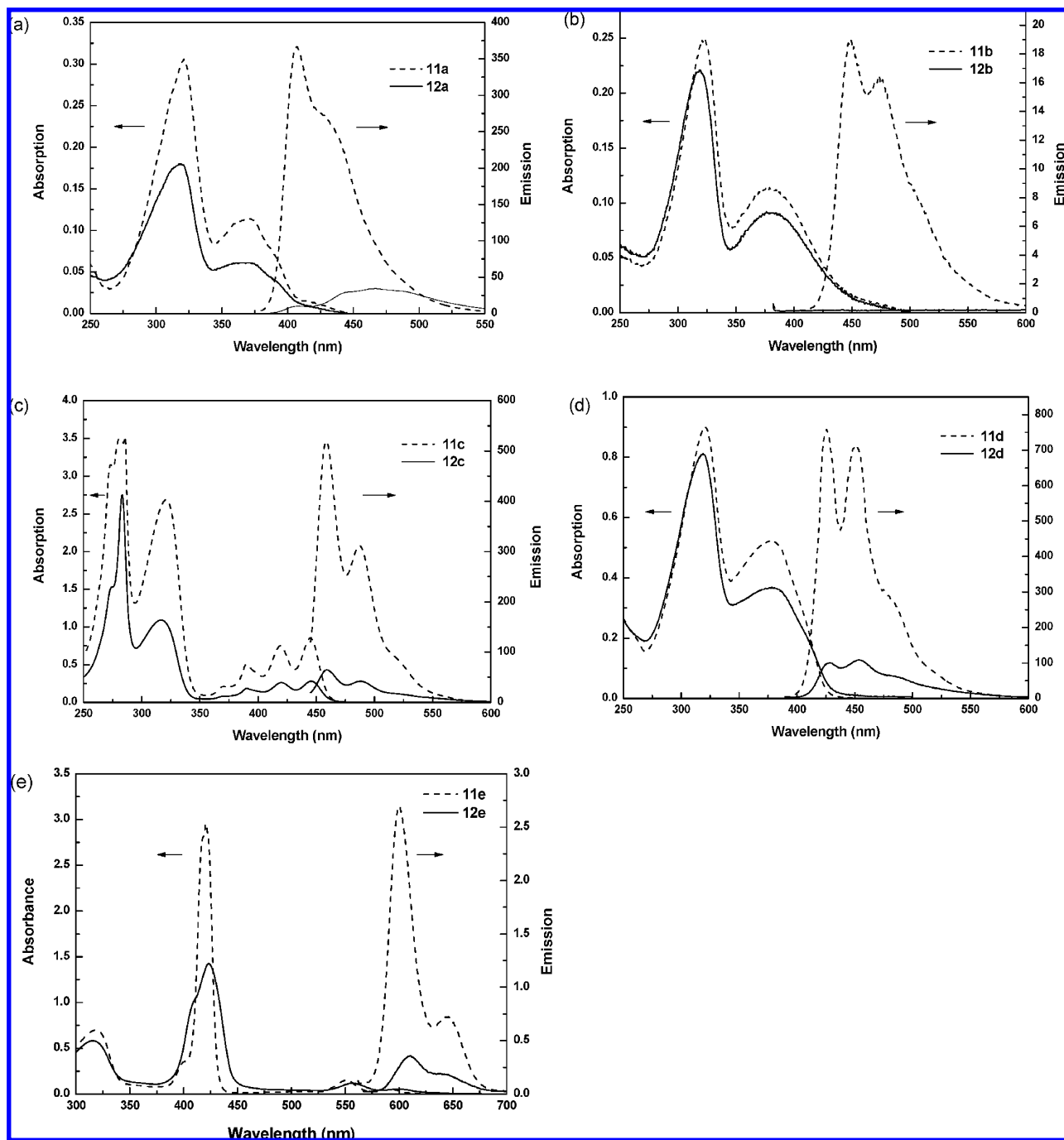


Figure 4. Absorption and emission profiles of **11** and **12** in CH_2Cl_2 .

As such the linkers in **12b** might orient toward a concave upward conformation so that the butyl substituents may be directed away from the graphite surface.²²

The images of **12d** were less self-explanatory. The separation of the two bright features (dashed rectangle in panel b₃ of Figure

3) was ~ 1.4 nm, which might be attributed to the benzene moieties at both ends of the oligoaryl linkers, while the dark region in between would be the central furan-benzene-furan module which might be away from the substrate and thus yield a smaller tunneling probability.^{22,23}

The X-ray structure of an alternating benzene-furan pentaaryl *anti*-**3d** showed an S-shape *anti*-conformation having two terminal benzene moieties (center-to-center) separated by ~ 1.5 nm (Figure S35).^{14,24} The center-to-center distance between two benzene rings in *syn*-**3d** could be estimated to be ~ 1.3 nm which

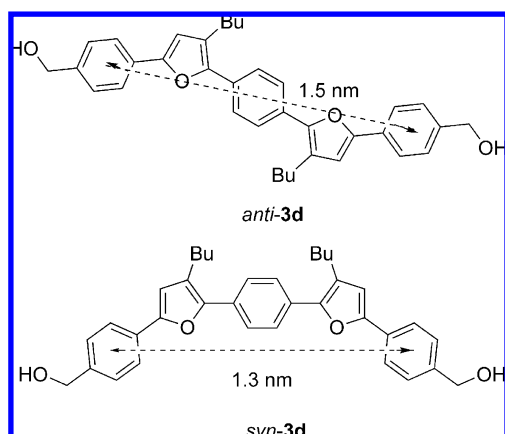
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(22) At this stage, the presence of possible *anti*-conformations for the linkers used in polymers **12b** and **d** could not be ruled out from the polymer products. Presumably, the interaction of these oligoaryl linkers having *anti*-conformation with the graphite substrate would be less favored than those having *syn*-conformation with HOPG, because the alkyl substituents in *anti*-conformation would be on both sides of the linkers.

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is comparable with the spacing between the two bright features for each of the monomeric units of **12d** in the STM images (panels b_1 and b_3 of Figure 3).

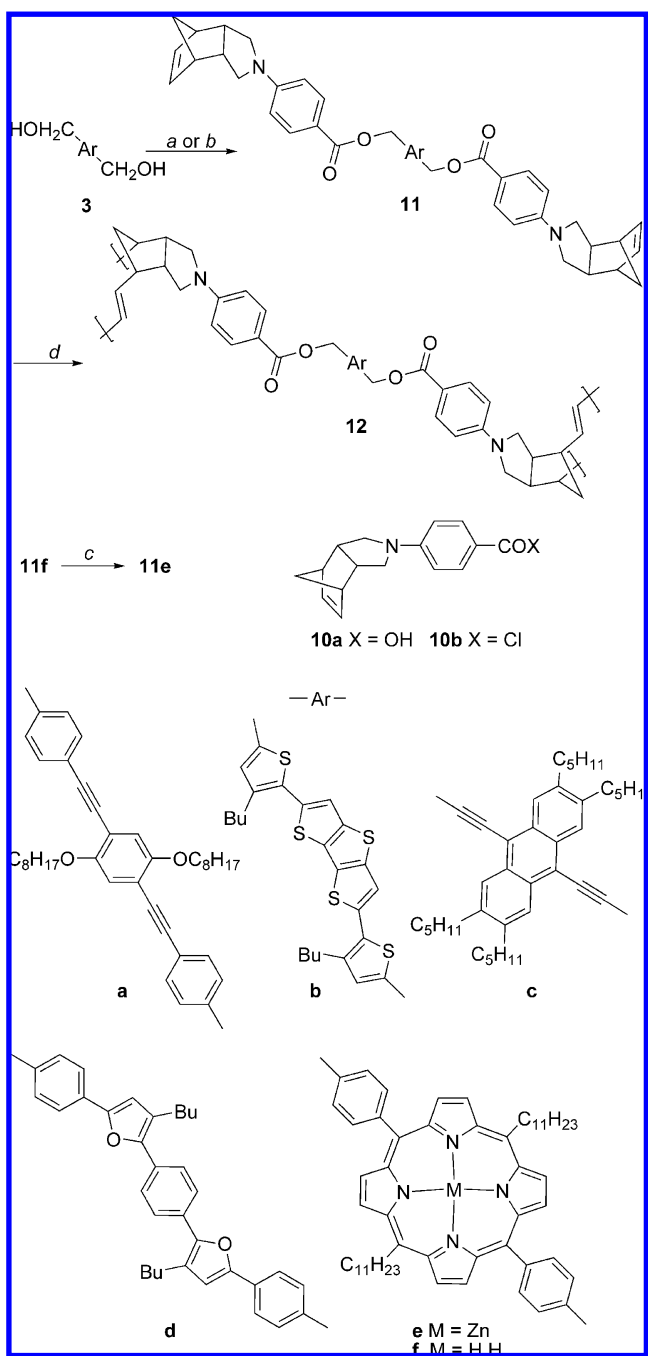


Since the space between the linkers was ~ 0.5 nm and the linkers are connected to the polymeric backbones via single bonds, rotation about these bonds might lead to multiple conformations resulting in obscure images measured by STM.

By adjusting the tunneling conditions, panels a_2 and b_2 of Figure 3 unveiled the unit cell vectors of the underlayer HOPG and thus the uniaxial commensuration of the corrugations of both **12b** and **d** with the [1340] direction of the HOPG substrate, demonstrating the contribution of substrate to the formation of the array assembly along the longitudinal axis. Attempts to obtain the similar STM images for other polymeric ladderphanes (**12a**, **c**, and **e**) were unsuccessful. It is noteworthy that long chain alkyl substituents are present on both sides of the linkers in these ladderphanes.²² It seems likely that interaction of these aliphatic chains with the graphite surface might not be strong enough to enable the formation of the assembled pattern as **12b** and **d** as shown in Figure 3.

Photophysical Properties. The absorption profiles for **12a–d** were similar to those of the corresponding monomers **11a–d** (Figure 4 and Table 1). The profiles for these polymers were essentially concentration independent. The extinction coefficients for these monomers **11** were larger than those contributed by each of the monomeric units of the corresponding polymers **12**. Because of the proximal distance between neighboring linkers (~ 0.5 nm) as described above, interactions between these chromophores may lead to a decrease in extinction coefficients. A similar observation was found in single-stranded polynorbornenes with coherently aligned pending chromophores.^{10,11}

It is striking to note that the Soret band for **12e** split into two bands at 407 and 421 nm, whereas there was only one band at 421 nm for **11e** (Figure 4e).²⁵ A similar observation was found in single-stranded polynorbornenes having the same porphyrin

Scheme 2^b

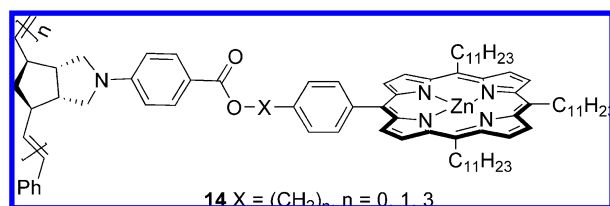
^b Reaction conditions: (a) **3a** or **3c**, and **10a**, PPh₃, DIAD, THF, rt (**11a**: 63%, **11c**: 21%); (b) **3b** or **3d** or **3e**, and **10b**, DMAP, Et₃N, CH₂Cl₂, rt (**11b**: 38%, **11d**: 87%, **11f**: 38%); (c) ZnOAc, MeOH, CH₂Cl₂, rt, 94%; (d) (C₆H₅)₂Cl₂Ru=CHPh, CH₂Cl₂, rt (**12a**: 87%, **12b**: 87%, **12c**: 81%, **12d**: 64%, **12e**: 80%).

chromophore **14** coherently aligned as pendants.¹¹ These results suggest that there might be exciton coupling between neighboring porphyrin linkers in **12e**, even though the spacings occupied by each of the monomeric units were ~ 5.5 Å.¹¹ It is known that intramolecular interactions between two porphyrin moieties leading to the splitting of the Soret band may depend on the distance and the dihedral angle between these two chromophores.^{11,26,27} Cofacial alignment of porphyrin chromophores in oligomers²⁶ and polymers²⁷ may occasionally facilitate such exciton coupling. In general, the exciton interaction between two porphyrins is relatively weak when the face-to-face distance

(25) The absorbances of **11e** were linearly related with concentration (10^{-6} – 10^{-5} M) and profiles remained unchanged, indicating that there would be no aggregation under these conditions (Figures S33, S34). These results suggest that the Soret band splitting in **12e** might have arisen from the locally high concentration due to the proximal distance between the porphyrin chromophores.

(26) For porphyrin containing oligomers, see: (a) Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454. (b) Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1006. (c) Osuka, A.; Liu, B.-I.; Maruyama, K. *J. Org. Chem.* **1993**, *58*, 3582. (d) Cho, S.; Yoon, M.-C.; Kim, C. H.; Aratani, N.; Mori, G.; Joo, T.; Osuka, A.; Kim, D. *J. Phys. Chem. C* **2007**, *111*, 14881. (e) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054.

of porphyrins in cofacial bisporphyrins was more than 0.5 nm.²⁸ A slight flexibility in the linker in **12e** might bring the neighboring porphyrin moieties closer leading to exciton coupling.^{11,29}



As shown in Figure 4 and Table 1, the intensities of the fluorescence spectra and the quantum yields (Φ_f) of **12** were much weaker than those of the corresponding monomers **11**. Except for **12a**, the emission profiles of **12b–e** are essentially similar to those of the corresponding monomers **11b–e**. Self-quenching might take place in polymers **12**, where intrachain interaction between chromophores might occur. These results are consistent with the double-stranded nature of **12**.

Time-Resolved Experiments. Time-resolved fluorescence decays for both monomers **11** and polymers **12** in CH₂Cl₂ were measured, and the results are also outlined in Table 1. Two-exponential fittings were used to obtain the fluorescence lifetimes (Figures S28–32). In addition to the longer lifetimes (τ) for **12b–e** which were comparable to those of **11b–e**, the shorter lifetimes were attributed to the self-quenching between neighboring chromophores. It is interesting to note that the lifetimes and their relative weights for **12e** were, for example, comparable with those of **14** which have coherently aligned

porphyrin pending groups in single-stranded polynorbornenes.¹² These results are consistent with the double-stranded structure having all neighboring linkers in close proximity.

As shown in Figure 4a, the emission of **12a** appears at a longer wavelength (473 nm) than those of **11a** (407, 428 nm). The lifetime of emission at 473 nm was 830 ps owing to the possible formation of an excimer-like species (Figure 4a). It is known that the orientation of participating chromophores would play an important role in the excimer formation.³⁰ The conjugated linker in **12a** is essentially linear, and the neighboring chromophores in **12a** might be nearly in an eclipsed relationship. No excimer-like emission was, however, observed for **12b–e**.

Conclusions

In summary, we have demonstrated a new class of polymers which have a double-stranded polybisenorbornene skeleton with multilayer planar oligoaryl linkers and are named as “polymeric ladderphanes”. Because of the ladder-like structure, all linkers are coherently aligned perpendicular to the longitudinal axis of the polymer. Strong interactions between these chromophore linkers have led to distinct photophysical characteristics. It is particularly noteworthy that these polymers can easily self-assemble to form an ordered pattern as shown in Figure 3. The use of this strategy for possible materials exploitation is in progress.

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Supporting Information Available: Experimental Section, ¹H and ¹³C NMR spectra of all new compounds, time-resolved fluorescence decay profiles of **11** and **12**, and the X-ray data of **3d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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