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Hexa-*peri*-hexabenzocoronene (HBC)-Incorporated Single- and Double-Stranded Polynorbornenes

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ABSTRACT: Double-stranded polymeric ladderphane **1** using HBC as linkers and the single-stranded comblike polynorbornene **2** with HBC pendants are synthesized by the ring-opening metathesis polymerization using the first-generation Grubbs catalyst. The photophysical properties of these HBC-incorporated polymers indicate significant interactions between adjacent polynuclear aromatic chromophores which are comparable with those of aggregated forms of the HBC cores. No liquid crystal properties, however, are observed in these polymers. The STM images of **1** and **2** demonstrate the unique properties of polynorbornene derivatives having *N*-aryl-5,6-endopyrrolidene pendants or linkers where the polymers are self-assembled to form ordered two-dimensional arrays on the HOPG surface.

Introduction

Well-defined nanosized polynuclear aromatic hydrocarbon derivatives are known to exhibit interesting electronic and self-assembly properties which offer tremendous opportunities for optoelectronic applications.[1] Two-dimensional graphene molecules such as hexa-*peri*-hexabenzocoronenes (HBCs) and homologues have extensively been investigated.[1a] Aggregation of these molecules via $\pi-\pi$ stacking renders some unique photophysical properties.[2] Thus, these disk-shaped molecules with flexible chains on the periphery readily form columnar mesophases[3] which can serve as nanowires for one-dimensional transport process along the column axes. The intrinsic high charge-carrier mobilities[4] qualify HBCs as particularly promising candidates for applications in field-effect transistors,[5,6] hole-conducting layers in photovoltaic devices,[6,7] or light-emitting diodes.[8] The presence of amino or ureido substituents on HBCs has been shown to enhance the aggregation tendency leading to form fluorescent organogels.[9] In addition, certain HBC derivatives can self-assemble to form graphitic nanotubes or coils.[10−12] Incorporation of these aromatic cores into polymers has been sporadically explored.[12,13] We recently reported a series of single- and double-stranded polynorbornenes by ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) of the corresponding monomers having a range of planar aromatic pendants or linkers.[14,15] Each of the monomeric unit in these polymers spans around 5.5 Å, and strong interactions between the pendants or linkers in these polymers readily take place as revealed by the significant reduction in fluorescence lifetimes and intensities in the emission spectra for the polymers in comparison with those for the corresponding monomers.[14,15] In addition, these polymers tend to self-assemble on the graphite surface to form an ordered two-dimensional array.[16] It is envisaged that the use of HBC moieties as the pendants or linkers in the corresponding single- and double-stranded polynorbornenes would generate a linear array of HBCs along the longitudinal axis of the polymers. We now wish to report the synthesis and photophysical propreties of HBC-incorporated polymeric ladderphanes **1** and the corresponding single-stranded polynorbornenes **2**.

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Results and Discussion

Synthesis. The HBC cores **3** and **4** were synthesized according to literature procedures.[3d] Esterification of **5**[17] with **6** afforded **7** in 85% yield. Sonogashira reaction of **3** with **7** gave monomer **8** in 65% yield. In a similar manner, **9** was obtained in 65% yield from **4** and **7**. Polymerization of **8** in the presence of the first-generation Grubbs catalyst **10** gave 70% yield of polymeric ladderphane **1**. Polymer **1** was sparing soluble in organic solvents. The low solubility was barely enough for photophysical measurements and scanning tunneling microscopic (STM) images as described below. Attempts to obtain the ^{1}H and ^{13}C NMR spectra for **1**, however, were unsuccessful. Polymer **2** was synthesized similarly in 90% yield from **9**. It is noteworthy that the chemical shifts of the aromatic protons in the HBC core of **2** appeared at higher field in comparison with those of the corresponding monomer **9**.[18]

Photophysical Properties. The absorption and emission spectra of **1** are compared with those of **8** in Figure 1. It is interesting to note that the β-band absorption for **1** slightly shifted to shorter wavelength (367 nm) in comparison with that of **8** (370 nm). In addition, the intensity of the β-band for **1** was also significantly reduced, whereas the absorbance around 320 nm for the aminobenzoate groups were similar for both **1** and **8**. This phenomenon appears to be typical for the aggregated HBC chromophores.[2e−g,9−12] The emission intensity for **1** was much weaker than that for **8**. In comparison with the emissions at higher energy (< 500 nm), the emission around 540 nm was relatively more prominent in **1** than that in **8**. Similar behavior was observed in the aggregated HBCs.[19] These results suggest that **1** might be consistent with the ladderphane structure because similar photophysical properties were found in related double-stranded polynorbornenes with planar oligoaryl linkers.[14d]

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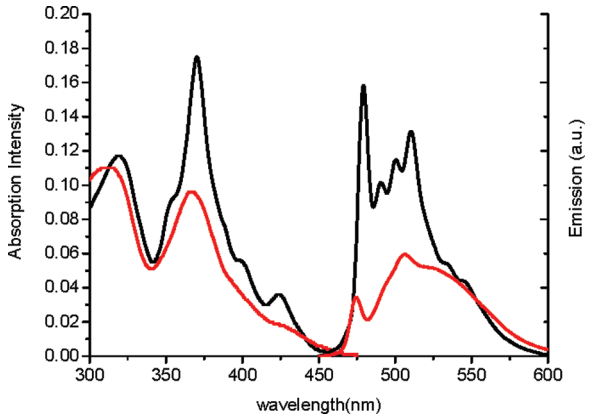
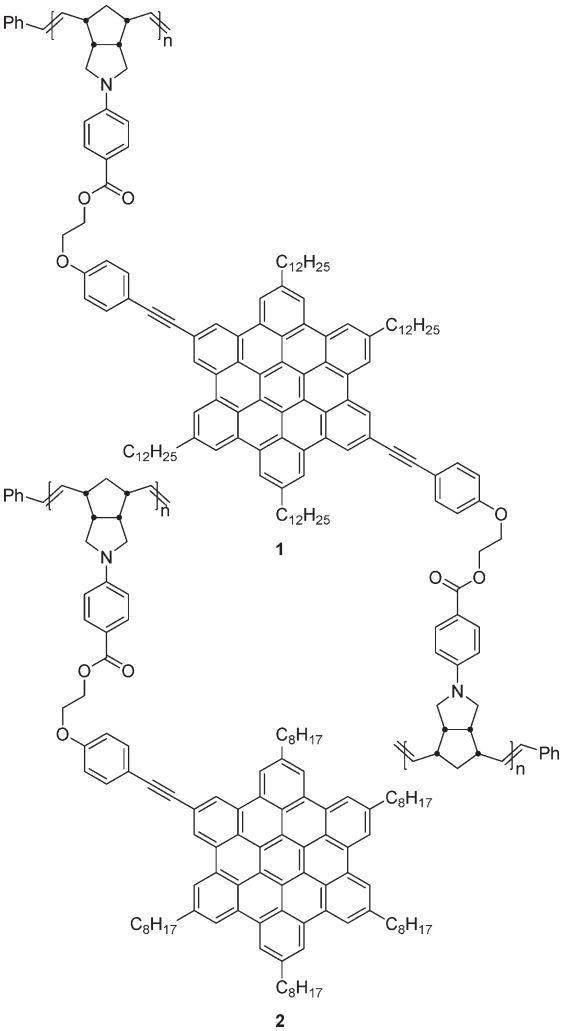
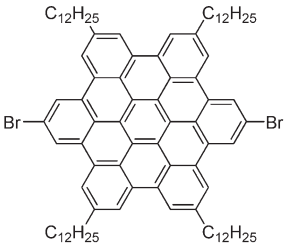
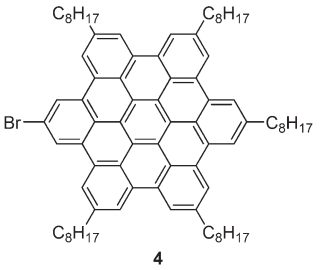


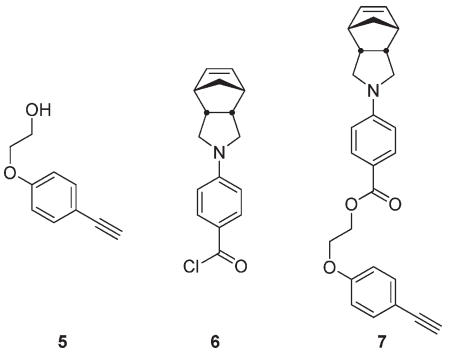
Figure 1. Absorption and emission spectra of **1** (red, saturated solution) and **8** (black, 1×10^{-6} M) in CH_2Cl_2.

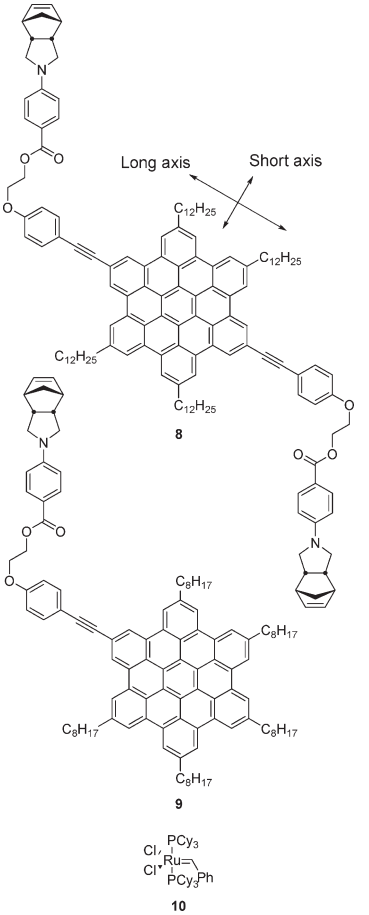
The photophysical properties of **2** behaved similarly (Figure 2). Again, the β-band absorption for **2** (367 nm) also blue-shifted with respect to those in **9** (370 nm). Moreover, the intensity of the emission around 540 nm relative to intrinsic emission for the HBC core in **2** (< 500 nm) also appeared to be enhanced with respect to those in **9**. These results are in agreement with the comblike structure for **2** where all the pendants are essentially aligned toward similar direction so that interaction between appended HBC moieties might take place.











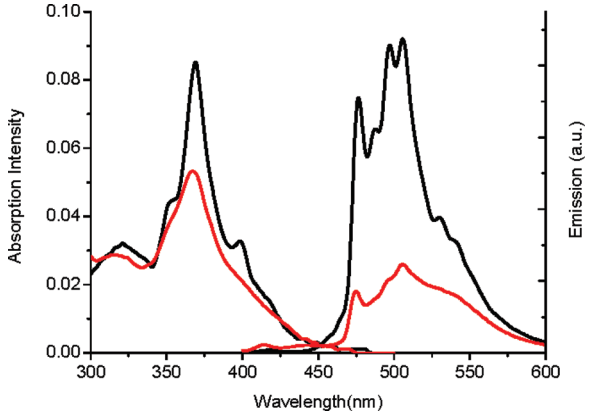


Figure 2. Absorption and emission spectra of **2** (red) and **9** (black) in 1,2-dichlorobenzene (1×10^{-6} M).

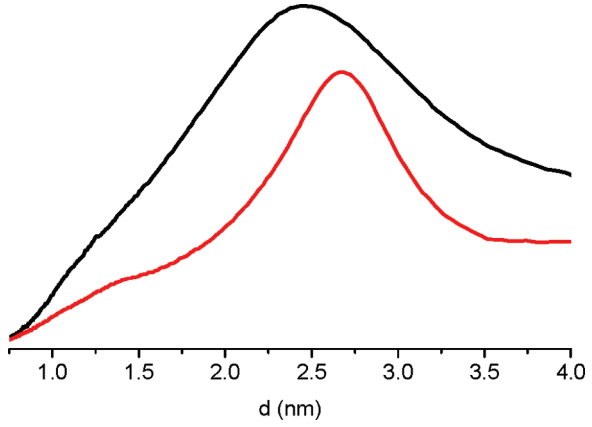


Figure 3. Scattered distribution vs *d*-spacing (nm) for **1** (black) and **8** (red) measured at ambient temperature.

X-ray Diffraction. Both monomer **8** and polymer **1** were subjected to the powder X-ray diffraction analysis, and the results are shown in Figure 3. It is worthy noting that both **8** and **1** exhibited broad peaks around 2.7 and 2.5 nm. Similar spacing is generally found in the solid of a range of symmetrically substituted HBC molecules.[20] These results indicate that **8** and **1** may exist long-range ordering with similar columnar packing as those of substituted HBCs.[20] It is known that certain substituted HBCs may display liquid crystal properties.[3] However, neither **8** nor **1** showed discrete liquid crystal phase as evidenced by the differential scanning calorimetry and polarized optical microscopic experiments.

STM Imaging. Figure 4 shows the STM images of monomers **8** and **9** and polymers **1** and **2** in phenyloctane on highly oriented pyrolytic graphite (HOPG) surface at the solid–liquid interface. Like those of substituted HBCs,[3d,21,22] **8** and **9** exhibited nicely ordered pattern with face-on morphology on HOPG. The unit cell parameters *a*, *b*, and α for the assemblies of **8** and **9** were 2.4 ± 0.2 nm, 2.8 ± 0.2 nm, $60 \pm 3°$ and 2.5 ± 0.2 nm, 2.6 ± 0.2 nm, $62 \pm 3°$, respectively. The lengths of unit cell vectors are longer than the nearest spacing of 1.47 ± 0.05 nm reported for the lattice of underivatized HBC monolayer on Au(111)[21a] and that of 1.93 ± 0.12 nm for hexakis(*n*-dodecyl)-*peri*-hexabenzocoronene (HBC-C12) monolayers on HOPG,[21b] ascribed to the effect of ethynylphenoxy side chains. It is interesting to note that the parameter *a* for **8** correlates quite well with the X-ray diffraction (XRD) data which reveal 2.7 nm for the intercolumnar distance for **8** as described above (Figure 3).

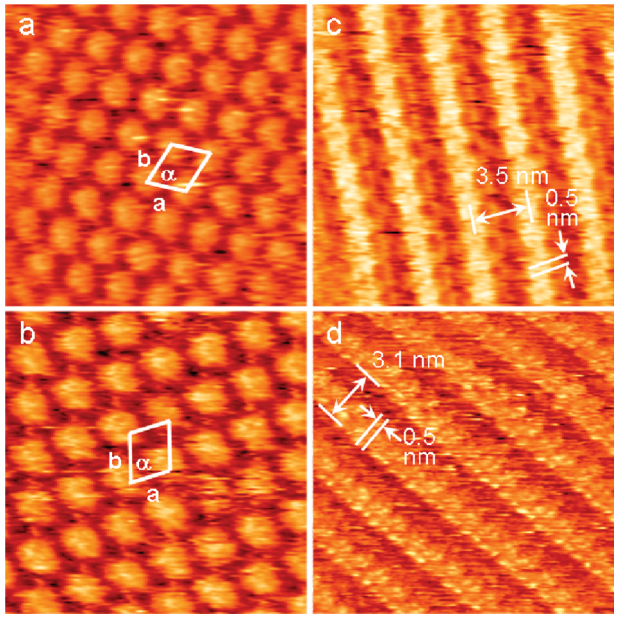


Figure 4. 16×16 nm STM images of monomers (a) **8** and (b) **9** and the correspondingly polymerized compounds (c) **1** and (d) **2** on HOPG. Unit cell parameters *a*, *b*, and α: (a) 2.4 ± 0.2 nm, 2.8 ± 0.2 nm, $60 \pm 3°$; (b) 2.5 ± 0.2 nm, 2.6 ± 0.2 nm, $62° \pm 3°$. Imaging conditions of E_{bias} and $i_{tunneling}$: (a) 0.40 V, 30 pA; (b) 0.60 V, 221 pA; (c) 0.68 V, 200 pA; (d) 0.60 V, 79 pA.

As shown in Figure 4, both polymers **1** and **2** are assembled nicely in a two-dimensional manner on HOPG. Like those of polymeric ladderphanes,[14] the rodlike polymers **1** and **2** may aggregate along the long axis of the polymer and form a one-dimensional assembly due to $\pi-\pi$ interaction between end groups (vinyl and styrenyl) of the polymers.[16] Presumably the spacing between the termini of two longitudinally interacting polymer molecules would be similar to those between the adjacent monomeric units in a polymer so that no apparent interstitial gap would appear along the longitudinal axis of the assembled polymers.[16] The spacing occupied by each of the monomeric units in these polymeric ladderphanes would be around 5–6 Å as revealed by the X-ray structure of a monomer.[15] Unlike polymeric ladderphanes with ferrocene linkers which are more rigid,[16] those with planar aromatic linkers tended to be more fluxional and no discrete monomeric units were observed. Such behavior was also found in the case of the images for **1** and **2**.

Both **1** and **2** are also assembled in the second dimension perpendicular to the longitudinal axis of the polymers. The widths of such assemblies (Figure 4c,d) for **1** and **2** were respectively 3.5 and 3.1 nm, somewhat larger than the unit-cell parameter *a* for monomers **8** and **9** (Figure 4a,b). In addition, the space 3.5 nm for **1** is also larger than that in the XRD results depicted in the previous section. Presumably, the orientation of the packing in powders and on HOPG surface may be different. Indeed, monomers **8** have two symmetric axes. The long axis includes the two norbornene moieties, whereas the short one is perpendicular to the long axis crossing the center of the HBC core. Similar axes can also be defined for **9**. It seems likely that the molecules are packed along the shorter axis in the STM images for monomers **8** and **9**. A similar packing pattern was supported in the XRD data of **1**. On the other hand, the widths of **1** and **2** on HOPG may behave like other single- and double-stranded polynorbornenes[14–16] by containing the polymeric backbones. Accordingly, the long axis would be responsible for the widths of these polymers. In this regard, the HBC linkers

may exhibit edge-on orientation by interacting with the graphite surface to enable self-assembly leading to the ordered pattern shown in Figure 4. The images for **2** shown in Figure 4d are worthy to comment. It seems likely that all these polymers are unilaterally oriented so that the polynorbornene backbones and the HBC pendants are aligned in alternative manner on HOPG.

Conclusions

In summary, we have demonstrated the first examples on the double-stranded polymeric ladderphanes using HBC as linkers **1** and the single-stranded comblike polynorbornene with HBC pendants **2**. The photophysical properties of these HBC-incorporated polymers have shown significant interactions between adjacent polynuclear aromatic chromophores which are comparable with those of aggregated forms of the HBC cores. However, no liquid crystal properties were observed in these polymers. The STM images of **1** and **2** again demonstrated the unique properties of polynorbornene derivatives having *N*-aryl-5,6-endopyrrolidene pendants or linkers where the polymers are self-assembled to form ordered two-dimensional arrays on the HOPG surface.[14−16]

Experimental Section

General. High-resolution mass spectrometric measurements were obtained from Jeol-JMS-700 mass spectrometry using the FAB method in 3-nitrobenzyl alcohol matrix. Gel permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515), and a refractive index detector (2414). THF was used as the eluent (flow rate = 1.0 mL/min). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determination of relative molecular weight using polystyrene as standard (M_n values ranged from 375 to 3.5×10^6). Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer.

2-Bromo-5,8,11,14,17-pentaoctylhexa-*peri*-hexabenzocoronene (4). In a manner similar to that described in the literature,[3d] to a solution of 4-bromo-4′,4″,4‴,4⁗,4⁗′-pentaoctylylhexaphenylbenzene[18] (200 mg, 0.17 mmol) in CH_2Cl_2 (87 mL) was added dropwise a solution of anhydrous $FeCl_3$ (1.2 g, 7.5 mmol) in nitromethane (30 mL). A nitrogen stream was bubbled into the reaction mixture throughout the entire reaction. The mixture was stirred for 5 h and quenched with methanol. The precipitate was filtered, washed with methanol, dried under reduced pressure, and chromatographed on silica gel (toluene) to afford **4** as a yellow powder (168 mg, 85%); mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/1): δ 0.81−0.95 (m, 15 H), 1.24−1.78 (m, 54 H), 1.79−1.83 (br, 4 H), 1.95−2.08 (br, 2 H), 2.40−2.60 (br, 4 H), 2.61−2.80 (br, 4 H), 2.91−3.00 (br, 2 H), 7.39 (s, 2 H), 7.53 (s, 2 H), 7.60 (s, 2 H), 7.74 (s, 2 H), 7.87 (s, 2 H), 8.00 (s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3/CS_2$ = 1/1): δ 14.4, 22.6, 23.1, 29.79, 29.88, 29.98, 30.02, 30.1, 30.26, 30.34, 30.5, 32.2, 32.4, 32.6, 36.5, 36.9, 37.2, 116.9, 117.2, 117.5, 119.3, 119.7, 119.8, 120.9, 121.2, 121.4, 126.2, 127.3, 127.4, 127.7, 128.0, 129.3, 137.8, 137.9, 138.0. IR (KBr): ν 3061, 2928, 2853, 1611, 1577, 1465, 1368, 1261, 1175, 1144, 1099, 1021, 859, 848, 804, 741, 722 cm^{-1}. HRMS (MALDI, M + H$^+$) calcd for $C_{82}H_{98}{}^{79}Br$ 1161.6852; found 1161.6860.

2-(4-Ethynylphenoxy)ethyl 4-(4-Azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)benzoate (7). To a CH_2Cl_2 (10 mL) solution of **5**[17] (230 mg, 1.4 mmol) and Et_3N (0.4 mL, 2.9 mmol) cooled to 0 °C under argon was added dropwise a solution of **6** obtained from corresponding acid[14a] and oxalyl chloride in CH_2Cl_2 (10 mL). The mixture was allowed to warm to rt and stirred overnight. The solvent and triethylamine were removed in vacuo, and the residue was chromatographed on silica gel (hexane/CH_2Cl_2 = 1/2) to give **7** as a white powder (480 mg, 85%); mp 202−204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, J = 8.4 Hz, 1 H), 1.62 (d, J = 8.4 Hz, 1 H), 2.95−3.00 (m, 5 H), 3.04−3.18 (m, 2 H), 3.25−3.36 (m, 2 H), 4.28 (t, J = 5.0 Hz, 2 H), 4.59 (t, J = 5.0 Hz, 2 H), 6.16 (s, 2 H), 6.37 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.85 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 45.4, 46.7, 50.5, 52.1, 62.3, 66.4, 75.8, 83.6, 110.8, 114.4, 114.5, 115.6, 131.3, 133.4, 135.6, 150.3, 158.8, 166.7. IR (KBr): ν 3265, 2956, 2923, 2852, 2103, 1693, 1605, 1525, 1505, 1471, 1456, 1384, 1277, 1248, 1178, 1124, 1106, 1065, 934, 831, 727 cm^{-1}. HRMS (MALDI, M + H$^+$) calcd for $C_{26}H_{26}NO_3$ 400.1913; found 400.1921.

Bisnorbornene Monomer 8. Under N_2, to a mixture of **3**[3d] (135 mg, 0.1 mmol), **7** (100 mg, 0.25 mmol), $Pd(PPh_3)_4$ (231 mg, 0.2 mmol), and CuI (38 mg, 0.2 mmol) in degassed piperidine/toluene (1/1, 4 mL) was refluxed for 16 h. After cooling, the solvent was removed in vacuo, and the residue was chromatographed on silica gel (CH_2Cl_2/EtOAc = 3/1) to afford **8** as a orange yellow solid (124 mg, 65%); mp > 300 °C (toluene). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, J = 7.2 Hz, 12 H), 1.00−1.75 (m, 76 H), 1.80−2.00 (br s, 8 H), 2.70−3.18 (m, 20 H), 3.22−3.36 (br s, 8 H), 4.38−4.44 (br s, 4 H), 4.62−4.78 (br s, 4 H), 6.16 (s, 4 H), 6.43 (d, J = 8.4 Hz, 4 H), 7.08 (d, J = 7.6 Hz, 4 H), 7.65−8.20 (m, 16 H, including 7.81 (d, J = 7.6 Hz, 4 H), 7.96 (d, J = 8.4 Hz, 4 H)), 8.20−8.30 (br s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.9, 29.6, 29.9, 30.0, 30.11, 30.16, 30.21, 30.4, 32.1, 32.5, 37.1, 45.5, 46.7, 50.5, 52.1, 62.6, 66.4, 89.0, 90.4, 110.9, 114.7, 115.8, 116.5, 117.8, 118.2, 119.6, 120.3, 121.5, 122.9, 127.7, 128.1, 128.5, 131.4, 133.3, 135.6, 138.9, 150.4, 158.5, 166.8. IR (KBr): ν 3056, 2922, 2851, 1706, 1604, 1521, 1508, 1458, 1372, 1273, 1246, 1178, 1104, 1062, 929, 865, 827, 767, 723, 698 cm^{-1}. HRMS (MALDI, M + H$^+$) calcd for $C_{142}H_{160}N_2O_6$ 1990.2354; found 1990.2382.

Norbornene Monomer 9. Under N_2, to a mixture of **4** (50 mg, 0.043 mmol), **2** (20 mg, 0.056 mmol), $Pd(PPh_3)_4$ (30 mg, 0.029 mmol), and CuI (2 mg, 0.01 mmol) in degassed piperidine/toluene (1/1, 7 mL) was refluxed for 28 h. After cooling, the mixture was quenched with water. The organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the residue which was chromatographed on silica gel (CH_2Cl_2/EtOAc = 50/1) to afford **9** as a yellow powder (56 mg, 65%); mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80−1.10 (m, 15 H), 1.20−1.80 (m, 52 H), 1.80−2.06 (m, 10 H), 1.80−2.20 (m, 16 H), 3.30−3.40 (m, 2 H), 4.38−4.46 (br, 2 H), 4.68−4.72 (br, 2 H), 6.18 (s, 2 H), 6.40 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 8.2 Hz, 2 H), 7.77 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 8.18−8.40 (m, 10 H), 8.60 (s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.5, 23.0, 29.9, 30.1, 30.5, 32.3, 32.6, 37.1, 37.3, 45.5, 46.8, 50.6, 52.2, 62.6, 66.6, 88.7, 90.5, 110.9, 114.8, 115.8, 116.7, 117.8, 118.1, 119.9, 121.7, 122.7, 125.0, 127.6, 128.4, 131.5, 133.2, 135.7, 138.6, 150.5, 158.6, 166.9. IR (KBr): ν 3060, 2955, 2923, 2852, 2201, 1706, 1605, 1582, 1508, 1464, 1375, 1274, 1247, 1179, 1105, 1071, 1036, 929, 862, 828, 802, 769, 722 cm^{-1}. HRMS (MALDI, M + H$^+$) calcd for $C_{108}H_{122}NO_3$ 1480.9425; found 1480.9431.

Polymeric Ladderphane 1. Under N_2, to a CH_2Cl_2 solution (20 mL) of **8** (20 mg, 0.01 mmol) was quickly added a solution of **10** (4.1 mg, 0.005 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at rt for 16 h, quenched with ethyl vinyl ether (2 mL), and further stirred for 2 h. The solution was concentrated, and the residue was filtered, collected, and dried to afford **1** (14 mg, 70%). IR (KBr): ν 3056, 2921, 2850, 1707, 1604, 1521, 1507, 1456, 1374, 1272, 1245, 1178, 1103, 1065, 865, 828, 767, 695 cm^{-1}.

Polynorbornene 2. In a manner similar to that described above, **9** (20 mg, 0.014 mmol) and **10** (2.7 mg, 0.0037 mmol) were transformed into **2** as a yellowish solid (19 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/1): δ 0.80−1.20 (br, 15 H), 1.20−2.20 (br, 62 H), 2.00−3.80 (br, 18 H), 4.10−4.80 (br, 4 H), 5.10−5.20 (br, 2 H), 5.20−5.40 (br, 2 H), 5.80−5.83 (br, 1 H), 6.10−7.20 (br, 8 H), 7.20−8.20 (br, 13 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 22.9, 29.8, 30.1, 30.4, 32.2, 32.5, 37.0, 37.2, 45.5, 45.9, 46.7, 50.5, 62.5, 66.5, 88.1, 90.6, 110.8, 114.7, 115.7, 116.6, 117.8, 118.0, 119.7, 121.4, 122.7, 127.5, 128.3, 131.4, 133.2,

135.6, 138.3, 150.4, 158.5, 166.8. IR (KBr): ν 3062, 2952, 2922, 2852, 2217, 1712, 1699, 1599, 1506, 1455, 1435, 1372, 1260, 1178, 1094, 1018, 861, 799, 768 cm^{-1}. GPC (THF): M_n = 6151, PDI = 1.14.

STM Imaging. The samples for imaging were prepared by placing on HOPG (highly orientated pyrolytic graphite, Advanced Ceramics, ZYH grade) an aliquot of 10 μL of **1**, **2**, **8**, or **9** in 1-phenyloctane with a micropipet. STM imaging was carried out with a PicoScan controller (4500, Agilent Technologies) at rt. The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments). Typical imaging conditions of bias voltage and tunneling current ranged from 0.4 to 0.7 V and from 30 to 300 pA, respectively. The images were raw data without flattening.

XRD of 1. The powder X-ray diffraction (XRD) experiments were carried out at beamline 17A in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The samples were packed into quartz capillary tube with 1 mm diameter. The wavelength applied to data collection was 1.3337 Å. The XRD data were collected by Mar345 imaging plate area detector with sample-to-detector distance at 280 mm. The 2-dimentional image was further integrated into 1-dimentional XRD pattern by the FIT2D program[23] with intensity distribution vs *d*-spacing. The scattering angle was calibrated by a mixture of silver behenate and silicon powder.

Acknowledgment. We thank the National Science Council and the National Taiwan University for support.

Supporting Information Available: Experimental procedures for the preparation of **11**−**16** and the ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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