

# Triple-Stranded Polymeric Ladderphanes

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ABSTRACT: The first triple-stranded polymeric ladderphanes **6** with multilayer planar oligoaryl linkers having  $C_3$  symmetry are synthesized by Grubbs I catalyst-mediated ring-opening metathesis of tris-norbornene derivatives **5**. All linkers are coherently aligned perpendicular to the longitudinal axis of the polymer. Interactions between these linkers lead to fluorescence quenching or perturbation of frontier orbitals, resulting in shift of the emission maximum. These triple-stranded polymeric ladderphanes tend to self-assemble to form an ordered pattern as revealed by TMAFM.

#### Introduction

We recently reported the first polynorbornene-based doublestranded polymeric ladderphanes 1 with a planar aromatic species or a ferrocene derivative as covalent linkers.<sup>1,2</sup> The key to the successful synthesis of these supramolecular scaffolds relies on the stereoselective Grubbs I catalyst-mediated ring-opening metathesis polymerization  $(ROMP)^3$  of bis-norbornene modules 2 connected by an relatively rigid linker (Scheme 1).<sup>1,2</sup> The presence of an N-arylpyrrolidine moiety endo-fused to the norbornene appears to be essential to control the stereoregularity (the stereochemistry of double bonds and the tacticity) of the double-stranded polymeric ladderphanes.<sup>1,2,4</sup> Presumably, the interactions between these aryl pendents would be responsible for the selectivity. Triple-stranded oligomers have been intertwined by means of metal coordination,<sup>5,6</sup> van der Waals interactions,<sup>7</sup> or hydrogen bonding.<sup>8–10</sup> More recently, triple-stranded DNA nanotubes are nicely constructed using different sizes of triangular building blocks covalently linked with three strands of DNA molecules.<sup>11</sup> To the best of our knowledge, triple-stranded polymeric ladderphanes with covalent linkers have not been known. It is envisaged that, with an appropriate design of covalent linkers, triple-stranded polymeric ladderphanes could be obtained by a similar strategy.

#### **Results and Discussion**

Synthesis. 1,3,5-Triphenylbenzene Linker. In the beginning of this research, reaction of  $3a^{12}$  with 4 under Mitsunobu conditions afforded the corresponding monomer 5a in 57% yield. ROMP of 5a with 30 mol % of the Grubbs I catalyst<sup>3</sup> afforded the corresponding triple-stranded polymer 6a in 85% yield  $(M_n = 13\,000, \text{PDI} = 1.61)$  corresponding to 12 repetitive units.<sup>13</sup> In the <sup>1</sup>H NMR spectrum, the olefinic protons shifted from  $\delta$  6.18 in 5a to a broad peak centered around  $\delta$  5.40 (overlapping with the absorption due to the benzylic protons) in 6a. The <sup>13</sup>C NMR spectrum of 6a is compared with that of 5a in Figure 1. The signals due to aromatic carbons in 6a appear at similar chemical shifts as those in 5a, whereas the



olefinic carbons shifted from  $\delta$  135 in **5a** to about  $\delta$  131.5 ppm in **6a**. The carbon signals in the high field region ( $\delta$  35–52 ppm), attributed to the carbons on the polymeric backbones and the pending pyrrolidine moieties, are fairly broad, presumably due to rigidity of the backbone in **6a**. Methanolysis of **6a** with NaOMe in MeOH/CHCl<sub>3</sub> afforded the single-stranded polymer isotactic **7** with all double bonds in trans configuration<sup>4</sup> in 77% isolated yield ( $M_n = 3700$ , PDI = 1.38) corresponding to 13 repetitive units. End-group analysis by <sup>1</sup>H NMR of a crude mixture from the methanolysis of **6a** suggests the degree of polymerization around 14.<sup>14</sup> The isolation of **7** in good yield with relatively narrow dispersity suggests that the polynorbornene strands in **6a** may have similar chain lengths and therefore be consistent with the triple-stranded structure (Schemes 2 and 3).

*Furan-Containing Oligoaryl Linkers with C*<sub>3</sub> *Symmetry.* Alternating benzene–furan oligomers have been shown to be highly fluorescent.<sup>15</sup> This kind of oligoaryl has been used as linkers for double-stranded ladderphanes, and the fluorescence of the conjugated chromophores has been significantly quenched.<sup>1</sup> It is envisaged that similar linkers could be used for the synthesis of triple-stranded ladderphanes. Thus, treatment of allenyllithium **11** (obtained from **12** with "BuLi) with **13** followed by TFA afforded **14** in 46% yield. Further reaction of **11** with **14** and then with TFA gave 30% yield of **15**, which was reduced with DIBAL-H to afford **3b** in 94%

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Figure 1. <sup>13</sup>C NMR spectra of (a) 5a, (b) 6a, (c) 5b, (d) 6b, (e) 5c, and (f) 6c in CDCl<sub>3</sub>.

yield. Mitsunobu reaction of **3b** with **4** gave **5b** in 52% yield (Scheme 4).

In a similar manner, sequential reaction of  $17^{15c}$  with <sup>*n*</sup>BuLi, 13, and TFA furnished 3c in overall 21% yield. Monomer 5c was obtained in 71% yield from the reaction of 3c with 4 under Mitsunobu conditions (Scheme 4). Polymerization of 5b and 5c using Grubbs I catalyst<sup>3</sup> and quenched with ethyl vinyl ether gave polymers 6b and 6c in 66 and 76% yields, respectively. The <sup>13</sup>C NMR spectra of 6b and c are also compared with those of 5b and c, respectively, in Figure 1.

Photophysical Properties. The photophysical properties of 5a-c and 6a-c are summarized in Table 1, and the emission spectra of 5a-c and 6a-c are shown in Figure 2. The quantum yields of the emission for polymers 6b and 6c were significantly reduced in comparison to those of the corresponding monomers 5b and 5c. These results indicate that, like double-stranded ladderphanes,<sup>1</sup> the adjacent linking chromophores in 6b and 6c should be in close proximity, and these polymers would be consistent with a triple-stranded structure. On the other hand, the quantum yields for 5a and 6a were comparable. It is interesting to note that the fluorescence spectrum of monomer 5a was completely different from that of 8a, but very similar to that of 10 (Figure 2d) due to 4-aminobenzoate chromophore. The charge transfer emissions of 5a and 10 appeared at longer wavelength than that of 9.<sup>16</sup> In addition, the luminescence spectrum of **6a** was almost identical to that of 7, but different from that of 5a. The emission of the triphenylbenzene linker in 6a may be buried in the emission of the aminobenzoate moiety. Polymer 7 is known to have all aminobenzoate pending groups aligned coherently toward the same direction, and the spacing occupied by each of the monomeric units is about 5.5 Å.<sup>4</sup> Interactions between adjacent pending aminobenzoate groups in 7 may perturb the frontier orbitals so that the photophysical properties may be different from those of the corresponding monomer **10**. It seems likely that the aminobenzoate moiety in **6a** may have similar environment to that in **7**. In other words, the aminobenzoate group in 6a may also be in close proximity to the neighboring aminobenzoate moieties. These results further suggest that **6a** would be a triple-stranded ladderphane.

Femtosecond laser equipped with a streak camera was employed to measure the time-resolved fluorescence decay of monomers **5** and polymers **6** in CH<sub>2</sub>Cl<sub>2</sub>. Single-exponential decay was observed for monomers **5b** and **5c** whereas twoexponential simulation was used to fit the fluorescence decay of polymers **6b** and **6c**. The results are summarized in Table 1. The longer lifetimes ( $\tau$ ) of polymers **6b** and **6c** are consistent with the lifetimes of the corresponding monomers **5b** and **5c**, and the shorter lifetimes were the major decay pathway (based on the relative weight) attributed to the self-quenching of the adjacent chromophores. These results further suggest that the chromophores aligned in **6b** and **6c** nicely in a triplestranded structure.

The emission of **5a** consisted of local emission of both triphenylbenzene and aminobenzoate moieties at 360 nm and charge separation emission at 464 nm. It would be difficult to monitor the actual mode of the decay pathway for **5a**. The situation with polymer **6a** would be more complicate because it may involve additional route of decay arisen from the interactions between adjacent chromophores.

**Tapping Mode Atomic Force Microscopic (TMAFM) Images.** Displayed in Figure 3 are TMAFM images of **6c** drop-cast on highly oriented pyrolytic graphite (HOPG). The length of the rodlike structure is at the scale of several hundred nanometers, which is much longer than a polymer molecule (10-mer is about 5 nm). Like those of double-stranded polybisnorbornenes,<sup>1,2</sup> the present result indicates that the assembly of the polymeric molecules may place on HOPG due to  $\pi-\pi$  attractions between end groups (vinyl and styryl) along longitudinal axis and van der Waals interactions between the neighboring polymeric backbones.

#### Conclusions

In summary, we have extended the strategy for double-stranded polybisnorbornenes to the synthesis of triple-stranded polymeric ladderphanes **6** with multilayer planar oligoaryl linkers having  $C_3$  symmetry. Because of the ladderlike structure, all linkers are coherently aligned perpendicular to the longitudinal axis of the polymer. Intrachain interactions between these linkers led to fluorescence quenching or perturbation of frontier orbitals, resulting in shift of the emission maximum. Like double-stranded



polymers, these triple-stranded polymeric ladderphanes can easily form an ordered pattern by self-assembly as depicted in Figure 3.









The use of this strategy for multiple stranded ladderphanes would be feasible and the application for materials research is in progress.

### **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) for **9a** and **9b**, and CHCl<sub>3</sub> was used as the eluent (flow rate, 1.0 mL/min) for **14**. 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  $3.5 \times 10^6$ ). Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500.

Synthesis of 5a. To a mixture of 4 (128 mg, 0.5 mmol),  $3a^{12}$  (50 mg, 0.13 mmol), and triphenylphosphine (164 mg, 0.63 mmol) in THF (15 mL) under argon cooled at 0 °C was added diisopropyl azodicarboxylate (126 mg, 0.63 mmol) in THF (3 mL) by a syringe pump over a period of 3 h. The mixture was warmed to room temperature (rt) and stirred for 36 h. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>:hexane = 2:1) to

substrate	$M_{\rm n}$ (PDI) or MW <sup>a</sup>	$\lambda_{\max}\left(arepsilon ight)^{b}$	$\lambda_{ m em}{}^c$	$\Phi_{\mathrm{f}}{}^d$	$\tau ({\rm wt} \%)$	$\lambda_{\rm em}^{e}$
5b	1475	318 (26)	399, 412	0.33	1350	390-410
6b	13000 (1.82)	318 (13)	406, 427	0.08	46 (72%), 1350 (28%)	390-410
5c	2070	387 (75)	431, 457	0.90	1100	430-460
6c	25000 (1.61)	387 (46)	440, 460	0.10	28 (71%), 1100 (29%)	430-460
5a	1108	260 (41) 321 (70)	360, 464	0.07		
6a	13000 (1.61)	260 (42) 315 (58)	358, 434	0.08		

Table 1. Photonhysical Properties of 5 and 6

<sup>*a*</sup> $M_n$  for polymers and molecular weight (MW) for monomers. <sup>*b*</sup> Absorption maximum and molar absorption coefficient (mM<sup>-1</sup> cm<sup>-1</sup>, based on the molecular weight of the monomeric unit) measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*c*</sup> Emission maximum in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*d*</sup> The quantum yields for **5b**, **6b**, **5c**, and **6c** in CH<sub>2</sub>Cl<sub>2</sub> were determined using cumarin I as a reference ( $\Phi_f = 0.99$ ), whereas those for **5a** and **6a** in CH<sub>2</sub>Cl<sub>2</sub> using 2,5-diphenyloxazole in cyclohexane ( $\Phi_f = 1.00$ ) as standard. <sup>*c*</sup> Monitoring wavelength for fluorescence decay.



Figure 2. Absorption and emission profiles of (a) 5b and 6b, (b) 5c and 6c, and (c) 5a and 6b in CH<sub>2</sub>Cl<sub>2</sub> (dotted, 5; solid line, 6). (d) Emission profiles of 5a (solid), 8 (dashed), 9 (dotted), and 10 (dash-dotted) in CH<sub>2</sub>Cl<sub>2</sub>.

afford **5a** as a white solid (79 mg, 57%); mp 190–192 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.52 (d, J = 8.3 Hz, 3 H), 1.62 (d, J = 8.3 Hz, 3 H), 2.95–2.99 (m, 12 H), 3.08–3.10 (m, 6 H), 3.27–3.32 (m, 6 H), 5.38 (s, 6 H), 6.17 (d, 6 H), 6.40 (d, J = 8.9 Hz, 6 H), 7.55 (d, J = 8.1 Hz, 6 H), 7.69 (d, J = 8.1 Hz, 6 H), 7.78 (s, 3 H), 7.94 (d, J = 8.9 Hz, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  45.4, 46.6, 50.5, 52.0, 65.5, 110.9, 116.1, 125.2, 127.4, 128.4, 131.4, 135.7, 136.3, 140.7, 142. 0, 150.6, 166.9. IR (KBr, cm<sup>-1</sup>): 3056, 2961, 2848, 1699, 1606, 1558, 1521, 1473, 1378, 1274, 1177, 1079, 985, 825, 767, 721. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>75</sub>H<sub>69</sub>O<sub>6</sub>N<sub>3</sub>: 1107.5186. Found: 2068.0513. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>75</sub>H<sub>69</sub>O<sub>6</sub>N<sub>3</sub>: 1107.5186. Found: 1107.5199.

Synthesis of 14. Under nitrogen, "BuLi (1.44 mL, 2.5 M in hexane, 3.6 mmol) was introduced dropwise to a solution of  $12^{15b}$  (1.12 g, 3.50 mmol) in THF (20 mL) at -78 °C, and the

mixture was stirred at -78 °C for 50 min. A solution of 1,3,5benenetricarboxaldehyde (164 mg, 1.00 mmol) in THF (10 mL) was then added at -78 °C, and the mixture was stirred at -78 °C for 1 h and then gradually warmed to rt. After further stirring for 1 h, TFA (0.5 mL, 6.0 mmol) was added, and the mixture was stirred at rt for 10 h. The mixture was quenched with saturated NaHCO<sub>3</sub> (30 mL), and the organic layer was extracted with Et<sub>2</sub>O (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried (MgSO<sub>4</sub>), filtered, and evaporated in vacuo to give the residue which was purified by flash column chromatography (silica gel, EtOAc/hexane 1:10) to afford **14** as a pale yellow solid (284 mg, 46%); mp 175–176 °C. IR (KBr):  $\nu$  2959, 2927, 2863, 1722, 1711, 1607, 1433, 1275, 1172, 1106, 769, 694 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.97 (t, J = 7.3 Hz, 6 H), 1.49 (sext, J = 7.3 Hz, 4 H), 1.72 (tt, J = 7.7, 7.3 Hz, 4 H),



Figure 3. TMAFM images of 6c on HOPG. Left: a 1  $\mu$ m × 1  $\mu$ m image shows that the rodlike feature extends over steps of HOPG. Right: a 300 nm × 300 nm image exhibits a close-packed monolayer of 6c.

2.79 (t, J = 7.7 Hz, 4 H), 3.92 (s, 6 H), 6.84 (s, 2 H), 7.78 (d, J = 8.4 Hz, 4 H), 8.06 (d, J = 8.4 Hz, 4 H), 8.10 (s, 2 H), 8.23 (s, 1 H), 10.14 (s, 1 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 22.8, 26.0, 32.1, 52.3, 111.7, 123.5, 124.9, 126.2, 127.5, 128.9, 130.3, 132.8, 134.4, 137.3, 147.6, 151.7, 166.9, 192.1. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>39</sub>H<sub>38</sub>O<sub>7</sub>: 618.2618. Found: 618.2620.

Synthesis of 15. Under nitrogen, "BuLi (0.48 mL, 2.5 M in hexane, 1.2 mmol) was introduced dropwise to a solution of 1215 (352 mg, 1.10 mmol) in THF (15 mL) at -78 °C, and the mixture was stirred at -78 °C for 50 min. A solution of 14 (618 mg, 1.00 mmol) in THF (10 mL) was added at -78 °C, and the mixture was stirred at -78 °C for 1 h and then gradually warmed to rt. After further stirring for 1 h, TFA (0.2 mL, 2.4 mmol) was added, and the mixture was stirred at rt for 10 h. The reaction was then quenched with saturated NaHCO<sub>3</sub> (30 mL), and the organic layer was extracted with  $Et_2O$  (3 × 100 mL). The combined organic extracts were washed with brine(100 mL), then dried (MgSO<sub>4</sub>), filtered, and evaporated in vacuo to give the residue which was purified by flash column chromatography (silica gel, EtOAc/hexane 1:10) to give 15 as a pale yellow solid (254 mg, 30%); mp 224-226 °C. IR (KBr): v 2952, 2928, 2871, 2851, 1719, 1607, 1434, 1274, 1175, 1107, 933, 769, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.98 (t, J = 7.3 Hz, 9 H), 1.50 (sext, J = 7.3 Hz, 6 H), 1.76 (tt, J = 7.7, 7.3 Hz, 6 H), 2.81 (t, J = 7.7 Hz, 6 H), 3.92 (s, 9 H), 6.84 (s, 3 H), 7.78 (d, *J* = 8.3 Hz, 6 H), 7.93 (s, 3 H), 8.05 (d, J = 8.3 Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 14.2, 22.9, 26.1, 32.2, 52.2, 111.5, 121.0, 123.0, 125.0, 128.3, 130.0, 131.8, 134.3, 148.4, 150.8, 166.5. HRMS (FAB<sup>+</sup>) m/zcalcd for C<sub>54</sub>H<sub>54</sub>O<sub>9</sub>: 847.3846. Found: 847.3838.

Synthesis of 3b. DIBAL (21.0 mL, 1.0 M in hexane, 21.0 mmol) was added slowly with stirring to a solution of 15 (847 mg, 1.00 mmol) in THF (20 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 2 h at rt, and then saturated NH<sub>4</sub>Cl (30 mL) was poured in slowly. The gel-like organic layer was then acidified with HCl (6 M, 30 mL) and extracted with  $Et_2O$  (3 × 200 mL). The combined organic layers were washed with saturated NaHCO<sub>3</sub> (2  $\times$  30 mL), brine (30 mL), dried (MgSO<sub>4</sub>), filtered, and evaporated in vacuo to give 3b as a pale yellow solid (720 mg, 94%); mp 183-185 °C. IR (KBr): v 3420, 2954, 2927, 1537, 1495, 1462, 1453, 1415, 1382, 1204, 1110, 1035, 1013, 935, 790 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (t, J = 7.4 Hz, 9 H), 1.45–1.60 (m, 6 H), 1.69–1.82 (m, 6 H), 2.84 (t, J = 7.6 Hz, 6 H), 4.73 (s, 6 H), 6.73 (s, 3 H), 7.40 (d, J = 8.0 Hz, 6 H), 7.74 (d, J = 8.0 Hz, 6 H) 7.94 (s, 3 H). <sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>): δ 14.5, 23.7, 26.9, 33.3, 64.7, 109.9, 121.4, 124.3, 125.7, 127.6, 130.4, 133.4, 143.4, 148.3, 153.3. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>51</sub>H<sub>54</sub>O<sub>6</sub>: 762.3920. Found: 762.3926.

**Synthesis of 5b.** To a THF solution (12 mL) of **3b** (200 mg, 0.26 mmol), **4** (345 mg, 1.3 mmol), and triphenylphosphine (345 mg,

1.3 mmol) under nitrogen at 0 °C was added diisopropyl azodicarboxylate (0.26 mL, 1.3 mmol) slowly. The mixture was warmed to rt and stirred for 24 h. Solvent was removed in vacuo, and the residue was washed by MeOH and EtOAc to afford **5b** (202 mg, 52%); mp 199–201 °C: IR (KBr):  $\nu$  3052, 2955, 2929, 1703, 1604, 1469, 1433, 1377, 1271, 1176, 1096, 934, 871, 762, 666 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.01 (t, J = 7.6 Hz, 9 H), 1.43–1.62 (m, 12 H), 1.72–1.90 (m, 6 H), 2.84 (t, J = 7.6 Hz, 6 H), 2.94–3.02 (m, 12 H), 3.04–3.11 (m, 6 H), 3.25–3.35 (m, 6 H), 5.32 (s, 6 H), 6.15 (s, 6 H), 6.38 (d, J = 8.8 Hz, 6 H), 6.72 (s, 3 H), 7.45 (d, J = 8.0 Hz, 6 H), 7.74 (d, J = 8.4 Hz, 6 H), 7.91 (d, J = 8.8 Hz, 6 H), 7.93 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 14.3, 22.9, 26.1, 32.3, 45.4, 46.7, 50.5, 52.1, 65.6, 109.4, 110.8, 116.0, 120.8, 123.6, 124.6, 128.3, 130.5 131.3, 132.0 135.6, 135.7, 147.6, 150.3, 151.7, 166.7. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>99</sub>H<sub>99</sub>-O<sub>9</sub>N<sub>3</sub>: 1474.7460. Found: 1474.7463.

Synthesis of 3c. Under nitrogen, "BuLi (3.8 mL, 2.5 M in hexane, 9.2 mmol) was introduced dropwise to a solution of 16<sup>15c</sup> (2.1 g, 4.3 mmol) in THF (100 mL) at -78 °C, and the mixture was stirred at -78 °C for 50 min. A solution of 1,3,5benenetricarboxaldehyde (164 mg, 1.00 mmol) in THF (10 mL) was added at -78 °C, and the mixture was stirred at -78 °C for 1 h and then gradually warmed to rt. After further stirring for 1 h, TFA (1 mL, 12 mmol) was added, and the mixture was stirred at rt for 10 h. The reaction was then quenched with saturated NaHCO<sub>3</sub> (100 mL), and the organic layer was extracted with EtOAc (3  $\times$  100 mL). The combined organic extracts were washed with brine (100 mL), then dried (MgSO<sub>4</sub>), filtered, and evaporated in vacuo to give the residue which was triturated with Et<sub>2</sub>O to give 3c as a yellow solid (281 mg, 21%); mp 203-204 °C: IR (KBr): v 3417, 3041, 2954, 2925, 2858, 1651, 1633, 1621, 1600, 1496, 1486, 1455, 1254, 1178, 1012, 832, 859, 834, 802, 734, 674, 667 cm  $^{-1}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 0.96 (t, J = 7.3 Hz, 9 H), 1.04 (t, J = 7.2 Hz, 9 H), 1.44–1.49 (m, 6 H), 1.52-1.60 (m, 6 H), 1.67-1.72 (m, 6 H), 1.79-1.85 (m, 6 H), 2.74 (t, J = 7.7 Hz, 6 H), 2.88 (t, J = 7.5 Hz, 6 H), 4.67 (s, 6 H), 6.68 (s, 3 H), 6.78 (s, 3 H), 7.37 (d, *J* = 8.2 Hz, 6 H), 7.70–7.77 (m, 12 H), 7.84 (d, J = 8.3 Hz, 6 H), 7.99 (s, 3 H). <sup>13</sup>C NMR (100 MHz, THF- $d_8$ ):  $\delta$  14.6, 14.8, 23.8, 24.0, 27.1, 27.2, 33.3, 33.5, 64.8, 110.1, 110.6, 121.7, 124.3, 124.7, 125.5, 126.0, 126.3, 127.5, 129.9, 130.3, 131.7, 133.4, 143.2, 148.3, 148.7, 153.1, 153.2. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>93</sub>H<sub>96</sub>O<sub>9</sub>: 1356.7054. Found: 1356.7084.

**Synthesis of 5c.** To a THF solution (12 mL) of **3c** (80 mg, 0.06 mmol), **4** (80 mg, 0.3 mmol), and triphenylphosphine (80 mg, 0.3 mmol) under nitrogen at 0 °C was added diisopropyl azodicarboxylate (0.06 mL, 0.3 mmol) slowly. The mixture was warmed to rt and stirred for 24 h. Solvent was removed in vacuo, and the residue was triturated with MeOH and EtOAc to afford **5c** 

(101 mg, 81%); mp 221–222 °C: IR (KBr):  $\nu$  3056, 2955, 2928, 2857, 1702, 1603, 1523, 1499, 1474, 1376, 1318, 1272, 1177, 1098, 934, 834, 810, 768, 721, 694, 673 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.98 (t, J = 7.2 Hz, 9 H), 1.04 (t, J = 7.6 Hz, 9 H), 1.44–1.82 (m, 30 H), 2.74 (t, J = 7.6 Hz, 6 H), 2.89 (t, J = 7.6 Hz, 6 H), 2.94–3.02 (m, 12 H), 3.04–3.11 (m, 6 H), 3.25–3.33 (m, 6 H), 5.31 (s, 6 H), 6.16 (s, 6 H), 6.39 (d, J = 8.8 Hz, 6 H), 6.67 (s, 3 H), 6.78 (s, 3 H), 7.44 (d, J = 7.8 Hz, 6 H), 7.71–7.76 (m, 12 H), 7.83 (d, J = 8.4 Hz, 6 H), 7.91 (d, J = 8.8 Hz, 6 H), 7.99 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 14.3, 22.8, 23.0, 26.1, 26.2, 32.1, 32.4, 45.4, 46.7, 50.5, 52.1, 65.6, 109.4, 109.6, 110.8, 116.0, 123.6, 123.7, 124.4, 124.8, 125.4, 128.2, 128.8, 130.2, 130.3 131.3, 132.1 135.6, 147.6, 150.3, 151.5, 151.7, 166.7. HRMS (FAB<sup>+</sup>) m/z calcd for C<sub>141</sub>H<sub>141</sub>O<sub>12</sub>N<sub>3</sub>: 2068.0515. Found: 2068.0513.

**Synthesis of 6a.** Under argon atmosphere, a solution of  $(Cy_3P)_2$ -Cl<sub>2</sub>Ru = CHPh (41.0 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added to **5a** (184 mg, 0.166 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred at rt for 3 h. The mixture was quenched with ethyl vinyl ether (2 mL). The mixture was concentrated and redissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The solution was poured into MeOH (20 mL). The resulting solid was collected by centrifuge to give **6a** (156 mg, 85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.68–2.10 (br, 6 H), 2.50–3.50 (br, 24 H), 5.4 (brs, 12 H), 6.57 (brs, 6 H), 7.50–7.80 (br, 15 H), 7.97 (brs, 6 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  44.52, 45.71, 46.29, 46.91, 65.87, 111.56, 116.82, 126.05, 127.42, 128.47, 131.45, 136.31, 140.76, 141.97, 150.87, 150.84, 166.50. IR (KBr, cm<sup>-1</sup>): 3027, 2933, 2852, 1705, 1605, 1521, 1374, 1270, 1178, 1096, 966, 824, 767, 697. GPC: PDI = 1.61,  $M_n = 13\,000$ ,  $M_w = 21\,000$ .

**Synthesis of 6b.** Under a nitrogen atmosphere, a solution of  $(Cy_3P)_2Cl_2Ru = CHPh (8.2 mg, 0.010 mmol) in CH_2Cl_2 (1 mL) was added to$ **5b** $(30 mg, 0.02 mmol) in CH_2Cl_2 (10 mL) and stirred at rt for 4 h. The mixture was quenched with ethyl vinyl ether (2 mL). The mixture was concentrated and redissolved in CH_2Cl_2 (1 mL). The solution was poured into MeOH (20 mL). The resulting solid was collected by centrifuge to give$ **6b** $(20 mg, 66%). IR (KBr): <math>\nu$  2953, 2930, 2857, 1720, 1606, 1523, 1497, 1479, 1453, 1433, 1376, 1271, 1178, 1096, 965, 934, 767 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl\_3):  $\delta$  0.70–1.00 (br, 9H), 1.20–1.97 (br, 18H), 2.45–3.60 (br, 30H), 4.80–5.65 (br, 12 H), 6.30–6.80 (br, 9H), 7.30–8.20 (br, 21 H). <sup>13</sup>C NMR (125 MHz, CDCl\_3):  $\delta$  4.0, 22.7, 25.9, 32.1, 37.5, 44.8, 46.7, 49.5, 65.7, 109.4, 111.4, 117.0, 123.8, 124.6, 126.1, 128.6, 130.5, 131.5, 135.7, 147.8, 151.0, 151.8, 166.7.  $M_n = 13000$ , PDI = 1.82.

**Synthesis of 6c.** Under a nitrogen atmosphere, a solution of  $(Cy_3P)_2Cl_2Ru = CHPh (11.0 mg, 0.013 mmol) in CH_2Cl_2 (1 mL) was added to$ **5c** $(90 mg, 0.045 mmol) in CH_2Cl_2 (10 mL) and stirred at rt for 4 h. The mixture was quenched with ethyl vinyl ether (2 mL). The mixture was concentrated and redissolved in CH_2Cl_2 (1 mL). The solution was poured into MeOH (20 mL). The resulting solid was collected by centrifuge to give$ **6c** $(69 mg, 76%). IR (KBr): <math>\nu$  2961, 2918, 2849, 1719, 1604, 1519, 1482, 1460, 1376, 1261, 1180, 1096, 1019, 964, 933, 861, 800, 662, 491 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl\_3):  $\delta$  0.70–1.15 (br, 18 H), 1.20–1.97 (br, 30 H), 2.35–3.50 (br, 36 H), 4.80–5.75 (br, 12 H), 6.30–6.80 (br, 12 H), 7.30–8.05 (br, 27 H). <sup>13</sup>C NMR (125 MHz, CDCl\_3):  $\delta$  13.9, 14.1, 22.6, 25.9, 31.9, 44.5, 46.3, 49.4, 65.8, 109.4, 111.5, 123.7, 124.6, 126.0, 128.6, 130.3, 131.5, 135.6, 147.5, 151.6, 166.6.  $M_n = 25000$ , PDI = 1.61.

Methanolysis of 6a. Under an argon atmosphere, a mixture of 6a (90 mg, 0.08 mmol) in CHCl<sub>3</sub> (20 mL) and 30% NaOMe in MeOH (10 mL) was stirred at rt for 20 h. Dichloromethane and water were added. The organic layer was separated and washed with H<sub>2</sub>O, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Ether (15 mL) was then added dropwise, and the residue was collected by centrifuge. The solid was washed several times with ether to give 7 (51 mg, 77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.40 (br, 1 H), 1.81 (br, 1 H), 2.74 (br, 2 H), 2.91 (br, 2 H), 3.24 (br, 4 H), 3.82 (br, 3 H), 5.34 (br, 2 H), 6.49 (br, 2 H), 7.87 (br, 2 H).

Under the same conditions, methanolysis of **6a** (15 g, 0.013 mmol) in  $CHCl_3$  (5 mL) and 30% NaOMe in MeOH (2 mL) gave

the residue which was analyzed by <sup>1</sup>H NMR for end-group analysis.<sup>14</sup>

AFM Characterization. TM-AFM measurements were carried out with a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA) using a  $10 \,\mu m$ scanner. The nominal curvature and the force constant for the cantilevers (NCHR, NanoWorld, Switzerland) were 10 nm and 42 nN/m, respectively. The sample, after being drop-cast with an aliquot of **6c** (50  $\mu$ L, 100 nM in CH<sub>2</sub>Cl<sub>2</sub>) on HOPG, was subjected to vacuum-drying and then imaged in a dry-N<sub>2</sub>(g) purged Plexiglas to minimize the effect of humidity on imaging.

**Time-Resolved Fluorescence Experiments.** A mode-locked Ti: sapphire laser (wavelength: 840 nm; repetition rate: 76 MHz; pulse width: <200 fs) passed through an optical parametric amplifier to produce 280 nm pulse laser. The fluorescence of sample was reflected by a grating (150 g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. The sample was prepared with  $1 \times 10^{-5}$  M concentration in CH<sub>2</sub>Cl<sub>2</sub> and using an ultra-microcuvette with 1 mm path length to maintain the excitation at the same time. The signal was collected for 20 times to decrease signal-to-noise ratio.

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of all new compounds (including end-group analysis for 7). This material is available free of charge via the Internet at http://pubs.acs.org.

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