Jacketed Poly(*p*-phenyleneethynylene)s: Nonaggregating Conjugated Polymers as Blue-Emitting Rods

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ABSTRACT: A series of dendronized poly(*p*-phenyleneethynylene)s were synthesized by the Pd-catalyzed coupling of a tetraphenylbenzene-substituted aromatic diiodide to 2,5-didodecyl-1,4-diethynylbenzene to form PPEs in excellent yield and high degree of polymerization. The tetraphenylbenzene-substituted monomer was obtained by a Diels-Alder reaction of a diethynylated arene with tetraphenylcyclopenta-dienone. The influence of the tether length (connecting the tetraphenylbenzene units to the main chain of the polymer) on the optical properties of the polymers was investigated. The closer the tetraphenylbenzene units were placed to the main chain, the larger is their effect upon the PPE's optical properties. In the case where the tether is shortest, i.e., two atoms, the optical properties of the PPE in the solid state and in solution are identical.

## Introduction

Dendronization or "jacketing" of conjugated polymers<sup>1–5</sup> is of great current interest as a means of their isolation from each other in solution and in the solid state. The isolation of single polymer chains will lead to materials that do not form excimers and aggregates in the solid state. Strategies that achieve the isolation of chromophores might lead to colorfast active materials for light-emitting diodes and potentially for polymer lasers. Issues that need to be dealt with are stability, electron transport, and charge carrier injection.

Poly(p-phenyleneethynylene)s (PPEs) are rigid-rod polymers with attractive optical properties.<sup>6,7</sup> Their chromic behavior and high quantum yield of fluorescence makes them useful in sensory and device applications.<sup>8,9</sup> While polyfluorenes grafted by Müllen dendrimers<sup>10</sup> have been reported,<sup>1,4</sup> there are no PPEs<sup>10</sup> known that are covered by these thermally stable, robust, and easy-to-make modules. However, Åida<sup>3</sup> has reported PPEs that were appended by Frechet's<sup>11</sup> benzyl ether dendrons. These polymers display intriguing photophysical and morphological properties. Densely dendronized PPEs show unity fluorescence quantum yields even in relatively concentrated solutions where interchain interactions play a significant role for the nondendronized PPE. Dendronization efficiently suppresses collisional deactivation of the excited state of the PPE. While Aida's experiments are elegant, the synthesis of Frechet-type dendronized PPEs is lengthy, and the benzylic groups of the Frechet dendrons are both thermally and hydrolytically sensitive. Müllen dendrimers,<sup>10</sup> on the other hand, are easily prepared and robust. We herein report the synthesis and properties of three different tetraphenylbenzene "minidendron"-substituted PPEs. Their aggregation and photophysical properties were investigated.

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**Figure 1.** Anisotropic displacement parameter (ADP) representations (50%) of the diynes **2** (top), **4** (middle), and **7** (bottom) in the solid state. The diyne **2** shows a perpendicular trans orientation of the two propargylic units with respect to the flat arene ring, while in **4** the side chains are coplanar to the arene ring and show a trans orientation of the methylene units as found in polyethylene. The monomer **7** shows a coplanar but helical arrangement of the side chains.

### **Results and Discussion**

Synthesis of the Monomers 3, 5, and 8. Starting from the diiodide 1, reaction with 2-(2-chloroethoxy)ethanol in the presence of an excess of potassium carbonate furnished 6 in 78% yield.<sup>9c</sup> An  $S_N 2$  reaction with 3-bromopropyne gave 7, while the reaction of 1 with 3-bromopropyne or 6-chlorohexyne under the same conditions led to the diynes 2 and 4. The three diynes (2, 4, 7) were subjected to a double Diels–Alder reaction

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**Figure 2.** ADP (50%) (top, left) representations of **3a**. The monomer has a step conformation (top right, van der Waals representation) that leads to an interesting (middle and bottom) solid-state arrangement, in which the phenyl rings of one tetraphenylbenzene substituent are interlaced with the ones from molecules of **3a** above and below.

with tetraphenylcyclopentadieneone to afford **3a**, **5**, and **8** in yields between 18% and 86%. Because of the presence of the oligoethylene chains, **8** smeared excessively on the chromatography support. It was difficult to remove small amounts of impurities, leading to the low yield for **8**. The other two monomers, **3a** and **5**, are obtained in excellent yields; **3a** was coupled under Pd catalysis to an excess of 2-methylphenylacetylene to give the fluorescent model compound **3b** in 88% yield after crystallization from dichloromethane and methanol.

To secure the structures of the diynes **2**, **4**, and **7**, single crystalline specimens were grown from their solutions in chloroform or dichloromethane. Figure 1 and Table 1 show the molecular structures and details of the structure analysis of the diynes in the solid state. In **2** the propargylic substituents are pointing in two different hemispheres, trans to each other. In **4** and **7** a more or less flat packing of the side chains is observed. The alkane chain in **4** takes up a perfect trans conformation, similar to that observed for methylene groups in polyethylene,<sup>12</sup> while in **7** the triethylene glycol chains adopt a more helical conformation, probably due to the presence of the oxygen atoms in the linker chain.

The bond lengths and bond angles of **2**, **4**, and **7** are in excellent agreement with the expected values for these unstrained compounds.

Growth of single crystalline specimen was attempted for 3a, 5, and 8. Alas, we were only successful in obtaining single-crystalline specimens from 3a and 5. The molecular structure and the packing of 3a are shown in Figure 2, and the pertinent crystallographic data are contained in Table 1. Single molecules of 3a are Z-shaped. This conformation leads to a solid-state arrangement in which the molecules are packed in an interdigitated zigzag motif (Figure 2, middle). If the view is rotated by 90°, the molecules are stacked on top of each other, tilted with the tetraphenylbenzene side chains interlocking (Figure 2, bottom). The central diiodoarenes are far removed from each other due to the bulky side chains and do not show any intermolecular contacts with other diiodoarenes. Bond lengths and bond angles are in excellent agreement with the expected values. In Figure 3, the single-crystal structure of 5 is shown. The three benzene rings are almost coplanar, and the four phenyl substituents are perpendicularly oriented around each of the outer phenyl rings. In the



**Figure 3.** ADP (50%) (top) representations of **5**. Bottom: Partial packing diagram of **5**. Partial interdigitation of the tetraphenylbenzene substituents of different molecules is visible.

solid state the tetraphenylbenzene substituents are interdigitated to give a better space filling. The crystal contains dichloromethane as a disordered solvent.

Synthesis and Characterization of the Polymers. With the monomers 3a, 5, and 8 available in gram quantities, the synthesis of conjugated polymers containing these modules was explored. The homopolymers, synthetically accessible by the reaction of 3a, 5, or 8 with acetylene gas in the presence of a Pd catalyst, would be too insoluble. A preliminary experiment with 3a confirmed our concerns, and an insoluble, infusible yellow material was obtained after removal of the solvents. However, copolymerization of 3a, 5, and 8 with a long-chain substituted diyne should give rise to the formation of soluble copolymers. The polycondensation of 2,5-didodecyl-1,4-diethynylbenzene with either 3a, 5, or 8 furnished the jacketed PPE derivatives 9, 10, and 11 in good to excellent yields with molecular weight ranging between  $3 \times 10^4$  and  $13 \times 10^4$  amu; **9–11** were amorphous according to powder diffraction experiments but showed a halo at approximately 20°, typical for  $\pi - \pi$ stacking interactions. The polymers did not show reversible phase transitions upon heating to above 150

°C; alas, slow decomposition occurred at that temperature, common for dialkoxy-PPEs. To have a nonjacketed PPE for comparison purposes, polymer **12** was prepared utilizing the same synthetic scheme. The material was obtained in an 83% yield as a yellow solid with an  $M_n$  of 56 × 10<sup>3</sup> and a PDI of 4.5. Table 2 shows the pertinent optical and molecular weight information of **9–12**.

**Optical Properties of the Polymers in Solution and in the Solid State.** In Table 2 and Figures 5–7 the optical properties of **9–12** in solution and in the solid state are shown. Polymer **12** is the PPE standard to which the other polymers are compared. Its absorption maximum in solution (Table 2) is 434 nm, typical<sup>6a</sup> for this substitution pattern. Its emission maximum in solution is at 456 nm. Upon going into the solid state, the absorption and the emission are red-shifted by 14 and 13 nm, respectively. Polymer **10** shows optical properties that are by and large very similar to those obtained for **12**. The shifts of emission and absorption when going from the dilute solution into the solid state are almost identical. The remotely placed tetraphenylbenzene unit in **10** therefore does not interfere with the





Scheme 2. Synthesis of the PPEs 9-12 by a Pd-Catalyzed Coupling





conformational freedom of the polymer chains; i.e., the twist angle between neighboring aryl rings is variable in solution like in **12**, and the polymer chains are planarized in the solid state. Polymers **9** and **11** show

a different spectroscopic behavior. Their absorption maximum in solution is somewhat blue-shifted, from 434 to 418 or 421 nm. A blue-shifted absorption in solution is unusual because it suggests that the rota-



**Figure 4.** X-ray crystal structure of **3b**. Top left: ADP (50%) representation of a single molecule of **3b**. Top right: view along the conjugated diphenylalkynylbenzene axis. Visible is the twist of one external phenylethynyl unit by 34° with respect to the central benzene ring. Bottom: packing of **3b** in the solid state. The phenyl groups of one molecule are in close contact to the tolyl group of a second one. The distance of the H atom of the phenyl ring to the center of the tolylethynyl ring is 3.12 Å.



**Figure 5.** Absorption and emission of the polymers **9–11** in chloroform.

tional freedom of the chains might be restricted toward a greater twist angle between neighboring phenyl rings.<sup>15–17</sup> To investigate this rarely observed behavior, the model trimer **3b** was prepared and suitable single crystals were obtained from hexafluorobenzene. Figure 4 shows an atomic displacement parameter (ADP) plot of **3b**. The bisphenylethynylbenzene unit is *not* planar in this structure, but one benzene ring is twisted by 34° (Figure 4) perhaps by the steric demand of the two bulky side groups. All of the hitherto reported bisphenylethynylbenznenes<sup>13</sup> are strictly planar in the solid state, regardless of their substitution pattern. Figure 4 shows



**Figure 6.** Absorption and emission of the polymers 9-11 in spin-cast films. The red-shifted shoulders are Raman-active states that are coupled to the excited state. The observed shifts are 905 cm<sup>-1</sup> for **9**, 1227 cm<sup>-1</sup> for **10**, and 1111 cm<sup>-1</sup> for **11**.

the packing of **3b** in the solid state. The conformation of the tetraphenylbenzene unit seems to dictate the packing of **3b** in the crystal. The molecules are stacked parallel in layers but shifted with respect to each other. In analogous polymers, the side chains therefore could influence the conformation of the main chain, leading to a permanently enforced twist. Close contacts between the central bisphenylethynylbenzene chromophores of different molecules do not exist. A similar situation was



**Figure 7.** Absorption and emission spectra of the model **12** in solution and in the solid state.

observed by Müllen, Setayesh, and Enkelmann for dendronized fluorenes.  $\!\!\!^4$ 

The absence of diffraction patterns in powders of **9–11** suggests that they all are amorphous. In **9** the chains of the polymers are probably well separated by

the bulky tetraphenylbenzene groups. An MM2 simulation (Figure 8) shows a space-filling view of a polymer chain of **9**. Two interesting features are visible. In the minimized ground state, the polymer backbone is not planar but twisted (top). The space-filling model (middle) demonstrates the sterically congested surrounding that will make a boardlike lamellar packing of the polymer chains difficult. The bottom of Figure 8 shows an endon view, demonstrating that the main chain is buried deeply beneath the substituents.

A quantum chemical analysis of the rotational energy potential around the two benzene rings was performed for the model dimer (Figure 9). Because of the size of the dimeric unit, it was only possible to perform the analysis on a semiempirical (AM 1) level. The use of AM1 can underestimate the barrier of rotation but tends to give satisfying qualitative results for carbon-based systems.<sup>12</sup> With AM1 a rotational barrier of only 0.2 kcal/mol is obtained for tolane, while Tour and Seminario determined a rotational barrier of 0.8 kcal/mol utilizing a sophisticated ab initio technique for the same molecule; AM1 results seem to err toward lower values.<sup>12b</sup> Investigation of the model dimer by AM1 shows a



Figure 8. MM2 calculations of an octameric model compound of polymer 9.



**Figure 9.** Rotational profile of a dimeric repeat unit of **9** (black squares) and of diphenylacetylene (blue triangles) as a model compound. The conformational analysis was performed utilizing SPARTAN with the AM1 basis set implemented on a windows platform. The *X*-axis represents the twist angle between the two arene rings, and the *y*-axis represents the relative energy (kcal mol<sup>-1</sup>).

complex rotational behavior. Contrary to diphenylacetylene, the dimer displays several maxima and minima (Figure 9). This rotational profile is a representative rotational profile but probably not the global minimum, despite the routine utilized to minimize all of the rotamers. Only a costly molecular dynamics calculation would give a complete picture of all low-energy rotational profiles accessible to this complex system. However, even with this relatively simple theoretical approach, the 90° conformation does not seem to be an energy maximum anymore, contrary to the case of tolane. The AM1 calculation of the dimer shows a complex rotational profile around the CC triple bond, suggesting that polymer 9 also is very "un-PPE-like" with respect to its conformational behavior.6c,12a The PPE 9 probably attains nonplanar conformations in both solution as well as in the solid state. The blue shift in the absorption of 9 in solution is therefore due to the preference of nonplanar lowest ground states.

The solution emission spectra of all of the polymers 9-12, on the other hand, are very similar. That can be understood because Sluch and Berg<sup>13</sup> and others<sup>14,15</sup> have demonstrated that after excitation of a octameric phenyleneethynylene model compound planarization of the backbone occurs to relax the first excited singlet state into its lowest, planar, state. The driving force for the planarization is considerably larger in the excited state than in the ground state due to the allenic resonance structures involved, leading to almost superimposable emission spectra for 9–12. The excited-state geometries of **9** and of **12** will resemble each other closely, despite their different rotational preference in the ground state. The observed shoulders in the fluorescence spectra of 9-12 in solution and in the solid state are due to the participation of Raman coupled states.<sup>18</sup>

Polymer **11** resembles **9**, while **10** has similar properties as the model polymer **12**. In the solid state **9** is attractive as its absorption does only shift by one nm when going from solution into the solid state. For the

other polymers a shift of 11–14 nm is observed when transitioning from solution into the solid state. Likewise, **9**'s emission is only slightly shifted when going from solution into the solid state. Polymer 11 shows unusual optical properties. Its bulky substituent is farthest away from the PPE backbone, but its optical properties resemble that of 9. We have attempted to perform polarizing microscopy and SEM on 11, but both methods only show the formation of smooth films. In addition, **11** is amorphous, so we could not obtain any meaningful powder X-ray diffraction data. As a consequence we are limited in our interpretation of the spectroscopic properties of 11. The-somewhat speculativeexplanation in its behavior might be gleaned from the packing of 7, which shows a helical coiling of the ethylene glycol side chains in the solid state. A second possibility is the obvious difference in the hydrophobicity/hydrophilicity of the connector compared to the tetraphenylbenzene "head". This might as well lead to a conformational distortion of the main chain in the solid state to best accommodate the packing of the whole object. To test this hypothesis, UV-vis and fluorescence spectra of 11 were recorded in a series of different solvents, however, without great effect. As a consequence, the reason for the changed optical properties in **11** is difficult to explain at the moment, but preparation of similar polymers with longer oligoethylene chains is planned in the near future to shed more light on this behavior.

# Conclusions

The novel dialkyl-co-dialkoxy-PPEs **9–12** were prepared. Polymers **9–11** carry tetraphenylbenzene substituents. If the bulky substituents are close to the main chain as shown in polymer 9 or attached by a hydrophilic linker (11) to the conjugated backbone, the optical properties of the PPE main chain are heavily influenced. The absorption and emission of 9 are blue-shifted in comparison to that of the model PPE 12. The reason for the blue shift is an increased twist of the main chain in solution and in the solid state and an insulation of the polymer chains from each other. This observation was corroborated by crystallographic studies on a tetraphenylbenzene-substituted bisphenylethynylbenzene derivative (3b) that showed a significant twist of a phenyleneethynylene group. Giving an overall selfconsistent picture, quantum chemical calculations suggest that polymers of the type 9 are not planar but have multiple conformational minima with respect to the rotation of two neighboring benzene rings in the conjugated main chain. Planarization of the backbone is therefore difficult to attain for 9.

### **Experimental Section**

**Instrumentation.** The <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Varian 300 MHz or a Bruker 400 MHz spectrometer using a broadband probe. The <sup>1</sup>H chemical shifts are referenced to the residual proton peaks of CDCl<sub>3</sub> at  $\delta$  7.24 (vs TMS). The <sup>13</sup>C resonances are referenced to the central peak of CDCl<sub>3</sub> at  $\delta$  77.0 and CDCl<sub>2</sub>CDCl<sub>2</sub> at  $\delta$  74.0 (vs TMS). Tetrachloroethane and chromium(III) acetylacetonate were used when obtaining <sup>13</sup>C NMR data for all polymers. UV–vis measurements were made with a Shimadzu UV-2401PC recording spectrophotometer. Fluorescence data were obtained with a Shimadzu RF-5301PC spectrofluorophotometer. A Headway Research model PWM32 instrument was used to spin-coat dilute chloroform solutions of polymers onto quartz slides for thin film experiments. 1,4-Diiodo-2,5-dihydroquinone,<sup>9c</sup> 2,5-didodecyl-1,4-di-

Table 1. Crystal Data and Unit Cell Parameters for the Compounds 2-5 and 7<sup>a</sup>

2 $C_{12}H_8I_2O_2$ (437.98) <i>P</i> -1 a = 4.2569(4) Å		7 $C_{20}H_{24}I_2O_6$ (614.19) P21/c a = 15.8462(9) Å	$\begin{array}{l} \textbf{3a} \\ C_{68}H_{48}I_2O_2 \\ (1150.9) \\ P21/n \\ a = 15.6063(10) \text{ Å} \end{array}$	5 $C_{74}H_{60}I_2O_2$ (1235.1) <i>P</i> -1 <i>a</i> = 12.560(2) Å	$\begin{array}{l} \textbf{3b} \\ C_{86}H_{62}O_2 \\ (1127.4) \\ P\text{-}1 \\ a = 14.259(2) \text{ Å} \end{array}$
b = 8.9180(8)  Å c = 8.9454(8)  Å $\alpha = 67.777(2)^{\circ}$ $\beta = 79.244(2)^{\circ}$ $\gamma = 82.963(2)^{\circ}$ $308.34(5) \text{ Å}^{3}$ 1	b = 13.7017(6)  Å c = 16.9431(8)  Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$ $\gamma = 90^{\circ}$ 1879.11(15) \text{ Å}^{3} 4	b = 7.6297(4)  Å c = 9.3907(6)  Å $\alpha = 90^{\circ}$ $\beta = 105.906(1)^{\circ}$ $\gamma = 90^{\circ}$ $1091.88(11) \text{ Å}^{3}$ 2	b = 8.9275(6)  Å c = 19.2262(13)  Å $\alpha = 90^{\circ}$ $\beta = 98.979(2)^{\circ}$ $\gamma = 90^{\circ}$ $2645.9(3) \text{ Å}^{3}$ 2	b = 12.952(2)  Å c = 23.031(3)  Å $\alpha = 84.628(3)^{\circ}$ $\beta = 81.298(2)^{\circ}$ $\gamma = 76.837(2)^{\circ}$ $3599.2(8) \text{ Å}^{3}$ 2	b = 15.310(2)  Å c = 17.941(2)  Å $\alpha = 75.054(3)^{\circ}$ $\beta = 78.969(2)^{\circ}$ $\gamma = 64.198(2)^{\circ}$ $3392.6 (8) \text{ Å}^{3}$ 2
2.359 mg/m <sup>3</sup> 5.081 mm <sup>-1</sup> 2788	1.846 mg/m <sup>3</sup> 3.351 mm <sup>-1</sup> 11439	1.868 mg/m <sup>3</sup> 2.912 mm <sup>-1</sup> 7165	1.445 mg/m <sup>3</sup> 1.235 mm <sup>-1</sup> 16828	1.272 mg/m <sup>3</sup> 1.041 mm <sup>-1</sup> 33301	1.104 mg/m <sup>3</sup> 0.064 mm <sup>-1</sup> 47536
1253	2073	1924	3485	10700	17018
[R(int) = 0.0195] R1 = 0.0165	[R(int) = 0.0279] R1 = 0.0201	[R(int) = 0.0292] R1 = 0.0189	[R(int) = 0.0514] R1 = 0.0541	[R(int) = 0.0693] R1 = 0.1695	[R(int) = 0.0534] R1 = 0.0809
wR2 = 0.0412 R1 = 0.0170 wR2 = 0.0415 0.582 and -0.410 e Å <sup>-3</sup>	wR2 = 0.0524 R1 = 0.0209, wR2 = 0.0530 0.566  and $-0.745 \text{ e} \text{ Å}^{-3}$	wR2 = 0.0474 R1 = 0.0196 wR2 = 0.0479 0.556 and -0.546 e Å <sup>-3</sup>	wR2 = 0.1256 R1 = 0.0705 wR2 = 0.1348 1.645 and -0.256 e Å <sup>-3</sup>	wR2 = 0.3945 R1 = 0.1866, wR2 = 0.4056 4.512 and -1.591 e Å <sup>-3</sup>	wR2 = 0.2259 R1 = 0.1181 wR2 = 0.2496 1.185 and -0.338 e Å <sup>-3</sup>
	2 $C_{12}H_8I_2O_2$ (437.98) P-1 a = 4.2569(4)Å b = 8.9180(8)Å c = 8.9454(8)Å $\alpha = 67.777(2)^{\circ}$ $\beta = 79.244(2)^{\circ}$ $\gamma = 82.963(2)^{\circ}$ 308.34(5)Å <sup>3</sup> 1 2.359 mg/m <sup>3</sup> 5.081 mm <sup>-1</sup> 2788 1253 [ $R(int) = 0.0195$ ] R1 = 0.0165 wR2 = 0.0412 R1 = 0.0170 wR2 = 0.0415 0.582 and -0.410 eÅ <sup>-3</sup>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

<sup>a</sup> Wavelength/temperature: 0.71073 Å at 150(2) K for 2, 3a, 4, and 7; 173(2) K for 3b and 5.

Table 2. Optical Properties and Molecular Weight Properties of Polymers 9-12

				absorption [nm]		emission [nm]		
	$M_{ m n}$	$\mathbf{P}_n^a$	PDI	$\lambda_{ m max\ solution}$	$\lambda_{ m max\ film}$	$\lambda_{ m max\ solution}$	$\lambda_{ m max\ film}$	
9	$29  imes 10^3$	42	2.5	418	417; $\Delta = 1 \text{ nm}$	453, 481	460, 480; $\Delta = 7 \text{ nm}$	
10	$13 imes 10^4$	179	4.3	437	445; $\Delta = 12 \text{ nm}$	456, 483	466, 492; $\Delta = 10 \text{ nm}$	
11	$74 imes 10^3$	98	9.9	421	432; $\Delta = 11 \text{ nm}$	449, 478	464, 472, 487; $\Delta = 15 \text{ nm}$	
12	$56  imes 10^3$	142	4.5	434	448; $\Delta = 14 \text{ nm}$	456, 483	469, 493, 516; $\Delta = 13 \text{ nm}$	

<sup>a</sup> Number of phenyleneethynylene units.

ethynylbenzene,<sup>19</sup> **6**,<sup>9c</sup> 1,4-diiodo-2,5-bisethylhexyloxybenzene,<sup>20,21</sup> and 2-ethynyltoluene<sup>22</sup> were prepared in accordance to published procedures.

Synthesis of 2. 1,4-Diiodo-2,5-dihydroquinone (20.3 g, 5.61 mmol), dimethylformamide (150 mL), potassium carbonate (9.31 g, 67.4 mmol), and propargyl bromide (18.7 g, 157 mmol) were placed in a 500 mL round-bottom flask and heated to reflux for 48 h. The mixture was allowed to cool to room temperature, and the solvent was removed. The crude product was dissolved in dichloromethane and washed with 1 N HCl and water. The organic layer was dried, the solvent was removed, and the crude solid was purified by chromatography on silica gel (3:7, ethyl acetate:hexane) to yield 2 as a colorless solid (23.3 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.376 (s, 2H), 4.697 (s, 4H), 2.556 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.604, 123.584, 85.819, 77.167, 76.120, 57.556. IR: v 616.70, 621.04, 627.79, 648.04, 662.50, 666.36, 678.90, 683.24, 689.02, 730.01, 736.76, 845.73, 851.51, 916.61, 921.43, 994.72, 1004.36, 1009.18, 1062.22, 1180.84, 1193.85, 1200.61, 1219.41, 1233.39, 1238.21, 1244.48, 1248.34, 1254.13, 1272.45, 1276.79, 1308.61, 1311.50, 1318.25, 1326.93, 1333.20, 1343.81, 1377.08, 1429.15, 1435.42, 1442.66, 1445.55, 1469.66, 2118.18, 2926.78, 2968.24, 3270.08, 3286.48, 3289.85. ES<sup>+</sup> MS (EI) calcd for [C<sub>12</sub>H<sub>8</sub>I<sub>2</sub>O<sub>2</sub>], 437.086, found 437.9; C, 32.91; H, 1.84; found C, 32.96, H, 2.01; mp 155 °C.

Synthesis of 1,4-Bis(2,3,4,5-tetraphenyl)benzyloxy-2,5diiodobenzene (3a). The diiododialkyne compound 2 (6.47 g, 14.8 mmol) *o*-xylene (20 mL), and tetraphenylcyclopentadienone (17.0 g, 44.2 mmol) were refluxed for 24 h. The solvent was removed under reduced pressure and the mixture purified by chromatography on silica gel (1:9, ethyl acetate:hexanes) to yield **3a** as a colorless solid (14.6 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.887 (s, 2H), 7.124 (m, 24H), 6.780 (m, 16H), 4.843 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  152.897, 141.378, 140.598, 139.73, 139.679, 139.496, 138.511, 132.925, 131.133, 130.932, 129.982, 129.64, 129.231, 127.169, 127.017, 126.388, 126.209, 126.121, 125.735, 125.424, 125.103, 86.749, 70.889. IR: v 744.53, 756.53, 831.26, 852.48, 893.94, 1029.43, 1062.22, 1200.61, 1214.59, 1349.11, 1381.42, 1439.76, 1462.19, 1549.70, 2902.19, 3023.69, 3044.91, 3056.48. MS (EI) calcd [ $C_{68}H_{48}I_2O_2$ ], 1150.17; found 1150.4; mp 298 °C.

Synthesis of Model Compound 3b. Diiodo monomer 3a (2.36 g, 2.05 mmol) and 1-ethynyl-2-methylbenzene (0.500 g, 4.30 mmol) were dissolved in dichloromethane (8 mL) and piperidine (8 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times after which  $(Ph_3P)_2Pd\breve{Cl}_2$  (71 mg, 0.102 mmol) and CuI (20 mg, 0.105 mmol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture was dissolved in dichloromethane and washed with 1 N HCl, 1 N NH4OH, and water. The organic layer was dried over MgSO<sub>4</sub> and the solvent removed. The resulting crude product was crystallized from a 1:1 mixture of dichloromethane and methanol to yield pure 3b (2.04 g, 88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.891 (s, 2H), 7.127 (m, 24H), 6.909 (m, 16H), 4.932 (s, 4H), 2.333 (s, 6H). <sup>13</sup>C NMR (TCE):  $\delta$  153.644, 141.653, 140.996, 140.308, 140.045, 139.954, 138.964, 133.979, 131.987, 131.856, 131.512, 131.299, 130.349, 129.995, 129.480, 128.357, 128.226, 127.397, 126.790, 126.487, 126.062, 125.496, 125.233, 123.413, 123.201, 118.560, 115.102, 115.091, 94.243, 90.037, 70.159, 20.464. IR: v698.18, 757.97, 894.91, 975.91, 1195.78, 1217.00, 1272.93, 1371.29, 1504.37, 1598.88, 1801.39, 1947.97, 2206.41, 2318.28, 2335.64, 2858.31, 2920.03, 3022.25, 3055.03. MS (FAB) calcd for [C<sub>86</sub>H<sub>62</sub>O<sub>2</sub>], 1126.47; found 1126.3; mp 235 °C.

**Synthesis of Polymer 9.** Monomer **3** (0.280 g, 0.200 mmol 0.244 mmol) and 2,5-didodecyl-1,4-diethynylbenzene (0.119 g, 0.200 mmol 0.257 mmol) were dissolved in dichloromethane (0.5 mL) and piperidine (0.5 mL) in an oven-dried Schlenk

flask. The flask was flushed with nitrogen, frozen, and evacuated three times after which (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> (1.4 mg, 2  $\mu$ mol), and CuI (0.4 mg, 2  $\mu$ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture dissolved in dichloromethane and washed with 1 N HCl, 1 N NH<sub>4</sub>OH, and water. The organic layer was dried over MgSO<sub>4</sub> and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield 9 (0.284 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.862 (m 2H), 7.009 (m, 24H), 6.753 (m, 16H), 4.839 (m, 4H), 1.542 (m, 8H), 1.148 (m, 28H), 0.823 (m, 6H). <sup>13</sup>C NMR (TCE):  $\delta$  152.977, 141.520, 140.827, 139.818, 138.860, 133.794, 132.099, 131.368, 130.225, 129.708, 129.278, 127.291, 126.665, 126.385, 125.962, 125.343, 125.130, 118.654, 115.006, 94.065, 90.965, 71.129, 34.180, 33.838, 31.674, 30.219, 29.073, 26.695, 22.985, 22.413, 13.823. IR: v 693.84, 698.18, 701.56, 742.54, 756.04, 766.17, 890.09, 999.06, 1012.56, 1025.10, 1027.51, 1054.51, 1069.94, 1195.30, 1198.68, 1340.43, 1374.19, 1429.15, 1439.76, 1447.48, 1451.82, 1469.17, 1496.18, 1599.36, 2848.67, 2902.67, 2912.79, 2918.58, 2952.81. GPC (polystyrene standards):  $M_n = 29350$ , PDI = 2.462.

**Synthesis of 4.** 1,4-Diydroxy-2,5-diiodobenzene (18.0 g, 49.7 mmol), potassium carbonate (41.8 g, 0.302 mol), and 6-chlorohexyne (24.2 g, 0.208 mol) were dissolved in dimethylformamide (200 mL). The mixture was heated to reflux for 48 h and allowed to cool to room temperature. The mixture was diluted with dichloromethane and washed with 1 N HCl (2 × 150 mL). The solvent was removed under vacuum, and the crude solid was purified by chromatography on silica gel (1:1, dichloromethane:hexanes) to yield **4** as a colorless crystalline solid (11.2 g, 43%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.151 (s, 2H), 3.922 (t, 4H), 2.254 (m, 4H), 1.890 (m, 6H), 1.724 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  152.500, 122.506, 86.168, 83.982, 69.502, 68.727, 28.109, 25.043, 18.152. IR: v 731.94, 999.54, 1001.95, 1032.33, 1207.36, 1349.11, 1398.30, 2110.46, 2800.56, 3089.27, 3263.81. MS (EI) calcd [C<sub>18</sub>H<sub>20</sub>I<sub>2</sub>O<sub>2</sub>], 521.96; found 522.1; mp 101 °C.

Synthesis of 5. Diyne 4 (0.826 g, 1.58 mmol) was dissolved in o-xylene (5 mL), and tetraphenylcyclopentadienone (5.00 g, 13.0 mmol) was added. The mixture was heated to reflux for 24 h and cooled to room temperature, and the solvent was removed. The crude solid was purified by chromatography on silica gel (2:8, ethyl acetate:hexanes) to yield 5 (1.45 g, 74%) as a colorless oil that solidified under high vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.432 (s, 2H), 7.020 (m, 24H), 6.727 (m, 16H), 3.714 (t, 4H), 2.575 (m, 6H), 1.731 (m, 4H).  $^{13}\mathrm{C}$  NMR (CDCl<sub>3</sub>):  $\delta$ 152.485, 141.829, 141.343, 140.402, 140.296, 139.962, 139.856, 139.264, 137.518, 131.431, 131.067, 130.278, 129.868, 129.807, 127.379, 127.212, 126.665, 126.316, 125.952, 125.254, 125.011, 122.279, 86.001, 69.608, 33.224, 28.883, 27.714. IR: v761.35, 1027.51, 1057.40, 1210.73, 1455.19, 1491.35, 1609.97, 1878.54, 1945.56, 2864.58, 2935.94, 3045.87. MS (EI) calcd [C<sub>74</sub>H<sub>60</sub>I<sub>2</sub>O<sub>2</sub>], 1234.27; found 1234.7; mp 86 °C.

Synthesis of Polymer 10. Diiodo compound 5 (0.101 g, 81.8  $\mu$ mol) and 2,5-didodecyl-1,4-diethynylbenzene (0.0380 g, 82.1  $\mu$ mol) were dissolved in tetrahydrofuran (0.2 mL) and piperidine (0.2 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which  $(Ph_3P)_2PdCl_2$  (6.3 mg, 9.0  $\mu$ mol) and CuI (1.7 mg, 8.9  $\mu$ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, the mixture dissolved in dichloromethane and washed with 1 N HCl, 1 N NH<sub>4</sub>OH, and water. The organic layer was dried and the solvent removed. The resulting polymer 10 was dissolved in dichloromethane and precipitated out of methanol three times and hexanes three times to yield 10 (74 mg, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.437 (m, 2H), 7.110 (m, 24H), 6.786 (m, 16H), 3.825 (m, 4H), 2.762 (m, 4H), 2.592 (m, 4H), 1.755 (m, 4H), 1.546, (m, 8H), 1.191 (m, 28H), 0.841 (m, 6H). <sup>13</sup>C NMR (TCE):  $\delta$ 153.77, 143.64, 142.21, 141.61, 140.59, 140.32, 139.16, 137.87, 133.23, 132.28, 131.67, 131.34, 129.54, 127.38, 127.24, 126.65, 126.33, 125.94, 125.20, 124.95, 123.77, 123.05, 120.39, 117.65, 114.90, 94.03, 90.86, 69.70, 44.70, 33.90, 33.49, 31.82, 30.45, 29.57, 29.22, 27.51, 22.55, 13.93. IR: v667.81, 694.81, 697.70, 794.62, 799.92, 1002.92, 1015.93, 1021.24, 1027.02, 1045.35, 1054.03, 1057.88, 1071.38, 1078.13, 1082.96, 1095.49, 1111.89, 1219.41, 1261.84, 2357.33, 2942.21, 3432.09. GPC (polystyrene standards):  $M_{\rm n}=13\times10^4,$  PDI = 4.3.

Synthesis of 7. Diiodo compound 6 (4.40 g, 8.18 mmol) was dissolved in dry tetrahydrofuran (25 mL), and under nitrogen purge NaH (0.665 g, 27.7 mmol) (80% in mineral oil) was added. 3-Bromopropyne (1.19 g, 10.0 mmol) was added, and the mixture was allowed to stir at room temperature for 24 h. The mixture was slowly poured onto water, and the precipitated solid was taken up in dichloromethane. The organic solution was washed with 0.5 N HCl (150 mL) and then with water. The organic layer was separated and dried. The solvent was removed and the crude solid purified by chromatography over silica gel (4:6, ethyl acetate:hexanes) to yield 7 as a colorless solid (3.62 g, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.212 (s, 2H), 4.211 (m, 4H), 4.072 (t, 4H), 3.850 (t, 4H), 3.774 (m, 4H), 3.697 (m, 4H), 2.406 (t, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  152.998, 123.396, 86.358, 79.588, 74.533, 70.832, 70.212, 69.518, 69.135, 58.398. IR: v 652.38, 656.72, 661.54, 666.84, 669.74, 678.41, 684.68, 694.81, 697.70, 700.59, 721.81, 725.18, 730.01, 799.92, 833.19, 841.39, 859.23, 877.55, 887.19, 918.54, 1000.50, 1015.93, 1025.58, 1033.77, 1051.13, 1066.08, 1086.33, 1087.78, 1101.28, 1121.05, 1136.96, 1219.41, 1232.91, 1243.04, 1265.70, 1286.43, 1330.31, 1353.45, 1355.86, 1427.71, 1435.42, 1437.83, 1445.55, 1450.37, 1455.67, 1463.87, 1466.28, 1486.05, 1492.80, 2830.34, 2837.09, 2849.63, 2861.68, 2879.04, 2884.35, 2895.44, 2920.99, 2929.19, 2935.94, 2944.62, 237.78, 3272.49. ES+ MS (EI) calcd [C<sub>20</sub>H<sub>24</sub>I<sub>2</sub>O<sub>6</sub>], 613.97; C, 39.11; H, 3.94; found 614.1; found C, 39.11; H, 4.02; mp 82 °C.

Synthesis of 8. Diiododiyne 7 (0.361 g, 0.588 mmol) was dissolved in o-xylene (10 mL), and tetraphenylcyclopentadienone (8.00 g, 20.8 mmol) was added. The mixture was heated to reflux for 48 h, cooled to room temperature, and the solvent was removed. The crude solid was purified by chromatography over silica gel (4:6, ethyl acetate:hexanes) to yield 8 (0.140 g, 18%) as an oil which solidified under high vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.695 (s, 2H), 7.055 (m, 24H),  $\check{6}$ .726 (m, 16H), 4.394 (s, 4H), 4.001 (t, 4H), 3.811 (t, 4H), 3.714 (m, 4H), 3.570 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 153.050, 141.858, 141.474, 140.048, 139.908, 139.372, 139.191, 135.479, 131.456, 131.233, 130.292, 129.929, 129.402, 127.504, 127.314, 126.833, 126.529, 126.294, 126.136, 125.502, 125.268, 123.397, 86.413, 77.327, 77.212, 77.010, 76.693, 71.450, 76.693, 71.450, 71.087, 70.205, 70.084, 69.500. IR: v 696.25, 701.56, 744.95, 763.28, 800.89, 1009.18, 1027.51, 1059.81, 1156.25, 1197.71, 1345.74, 1432.53, 1441.69, 1447.48, 1456.16, 1480.75, 1495.21, 1575.25, 1598.40, 1709.30, 2846.25, 2926.78, 3019.84, 3051.18. ES+ MS (EI) calcd [C<sub>76</sub>H<sub>64</sub>I<sub>2</sub>O<sub>6</sub>], 1326.28; C, 68.78; H, 4.86; found fragmentation: 552.2, 408, 262.9; found C, 68.72; H, 5.06; mp 126 °C.

Synthesis of Polymer 11. Diiodo compound 8 (0.134 g, 101  $\mu$ mol) and 2,5-didodecyl-1,4-diethynylbenzene (47.0 mg, 0.101 mmol) were dissolved in tetrahydrofuran (0.1 mL) and piperidine (0.1 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which  $(Ph_3P)_2PdCI_2$  (0.7 mg, 1  $\mu$ mol) and CuI (0.2 mg, 1  $\mu$ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, and the mixture dissolved in dichloromethane and washed with 1 N HCl, 1 N NH<sub>4</sub>OH, and water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed. The crude polymer was dissolved in dichloromethane and precipitated out of hexane and then acetone to yield 11 (93 mg, 60%) as a dark yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.648 (m, 2H), 7.048 (m, 24H), 6.724 (m 16H), 4.330 (m, 4H), 3.373 (m, 16H), 2.442 (m, 4H), 1.638 (m, 4H), 1.525 (m, 8H), 1.198 (m, 28H), 0.829 (m, 6H). <sup>13</sup>C NMR (TCE): *d* 153.867, 142.047, 141.643, 140.703, 140.207, 140.192, 140.146, 139.550, 139.368, 135.465, 132.381, 131.663, 131.350, 130.511, 130.005, 129.419, 127.478, 127.205, 126.729, 126.487, 126.234, 126.052, 125.425, 125.172, 94.809, 90.564, 71.595, 71.524, 70.988, 70.594, 70.058, 69.815, 69.735, 44.771, 34.023, 31.91, 30.555, 29.635, 29.483, 29.251, 22.658, 22.426, 22.274, 14.024. IR: v 617.66, 667.81, 694.81, 697.70, 718.92, 751.70, 897.80, 1053.06, 1061.74, 1094.53, 1117.67, 1125.39, 1142.74, 1258.47, 1439.76, 1460.01, 2363.60, 2943.65, 3402.20, 3537.69. GPC (polystyrene standards):  $M_n = 73780$ , PDI = 9.9.

Synthesis of Polymer 12. 2,5-Bisethylhexyloxy-1,4-diiodobenzene (0.400 g, 0.682 mmol) and 1,4-diethynyl-2,5-didodecylbenzene (0.319 g, 0.689 mmol) were dissolved in tetrahydrofuran (1.5 mL) and piperidine (1.5 mL) in an oven-dried Schlenk flask. The flask was flushed with nitrogen, frozen, and evacuated three times, after which (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> (4.8 mg, 6.8  $\mu$ mol) and CuI (1.3 mg, 6.8  $\mu$ mol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed, the mixture dissolved in dichloromethane and washed with 1 N HCl, 1 N NH<sub>4</sub>OH, and water. The organic layer was dried over MgSO<sub>4</sub> and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of hexane and then acetone to yield 12 (0.449 g, 83%) as a dark yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.362 (m, 2H), 6.979 (m, 2H), 3.887 (m, 4H), 3.176 (m, 4H), 1.907 (m, 4H), 1.500 (m, 2H), 1.222 (m, 52H), 0.849 (m, 18H). <sup>13</sup>C NMR  $(CDCl_3)$ :  $\delta$  153.659, 141.901, 132.261, 122.820, 116.623, 114.144, 94.026, 90.751, 71.985, 39.589, 30.549, 29.666, 29.612, 29.529, 29.306, 29.117, 23.917, 23.041, 22.618, 14.001, 11.129. IR: v679.86, 717.95, 858.75, 883.82, 989.41, 1050.65, 1210.73, 1277.75, 1464.83, 1516.91, 2163.02, 2854.93, 2940.28, 3841.94. GPC (polystyrene standards):  $M_n = 56\ 434$ , PDI = 4.461.

**Differential Scanning Calorimetry Measurements.** DSC measurements were taken on a Mettler Toledo DSC 822. The samples were weighed into a 40  $\mu$ L aluminum crucible, and the lid was punctured. Each sample was heated from 25 to 250 °C at a rate of 10 °C/min under N<sub>2</sub>.

**X-ray Powder Diffraction Measurements.** The X-ray powder diffraction data were collected on a Rigaku powder X-ray diffractometer using a Bragg–Brentano geometry with Cu K $\alpha$  radiation. The step scan covered the angular range 5–50°  $2\theta$  in steps of 0.02°.

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**Supporting Information Available:** CIFs, crystallographic tables, and experimental details for the single-crystal X-ray structure determination for **2**, **3a**, **3b**, **4**, **5**, and **7**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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