Aza-Wittig Polymerization: A Simple Method for the Synthesis of Regioregular Poly(azomethine)s

Junpei Miyake and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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ABSTRACT: Fully regioregular π-conjugated poly(azomethine)s (**9a**−**d**) were successfully synthesized via aza-Wittig polymerization from an AB monomer system. The obtained regioregular poly(azomethine)s showed moderate solubility in common organic solvents such as $CHCl_3$, THF, and toluene. In the UV−vis absorption spectra, polymer **9c** displayed absorption maximum of the longer wavelength at 425 nm and a large red shift of 95 nm relative to the absorption maximum of the model compound **14** (λ_{max} = 330 nm) in dilute $CHCl_3$ solution, indicating the extension of the π-delocalization length of polymer **9c** via the AB-type π-conjugated poly(azomethine) backbone. In the solid state, UV−vis absorption spectra and XRD data revealed that these regioregular poly(azomethine)s have higher crystallinity values compared to those for the regiorandom poly(azomethine)s.

Introduction

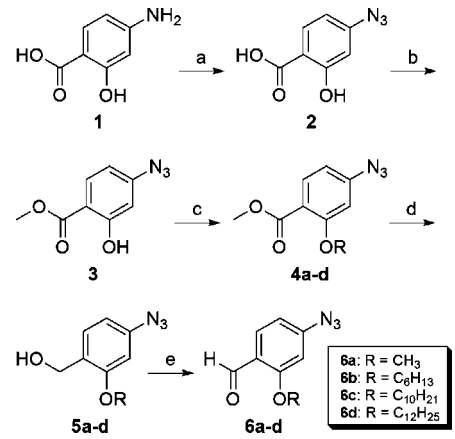
The chemistry of regioregular π-conjugated polymers has recently received considerable attention and been expanding because such polymers can self-assemble into highly ordered supramolecular architectures in the solid state. Crystalline packing of the regioregular polymers gives self-ordering of the conjugating polymer chains in the films, leading to enhanced light absorptions and higher charge carrier mobilities desirable for various optoelectronic device applications including organic field effect transistors and photovoltaic cells. A typical example of the importance of polymer microstructure as it pertains to physical properties can be illustrated with poly(3-alkylthiophene)s (PATs). By controlling the relative position of the alkyl pendant groups through a regiochemical synthetic manner, PATs self-assemble into highly ordered two- and three-dimensional assemblies which display various notable properties. For example, highly regioregular, head-to-tail coupled, poly(3-alkylthiophene)s (HT−PATs) possess higher crystallinity, nonlinear optical responses, greater electrical conductivity, a smaller bandgap, and greater field effect charge mobility than the regiorandom/regioirregular analogues.[1] However, despite the well-known influence of regiochemical arrangement of side chains on the properties of PATs, such control of molecular structure is not common for other classes of π-conjugated polymers.[2]

Aromatic poly(azomethine)s,[3] often termed poly(Schiff base)s, have been generally recognized as a special class of high-performance polymers due to their prominent properties such as excellent thermal stability,[4] the ability to chelate with metals,[4] electrical conductivity,[5] second- and third-order nonlinear optical properties,[6] and fiber-forming property.[7] In general, the basic methodology for the synthesis of poly(azomethine)s is based upon the condensation reaction of AA/BB monomers: a dialdehyde and a diamine. To date, several types of A_2B_2 poly(azomethine)s have been prepared by this method.[8] However, this type of polycondensation system is not appropriate for preparing poly(azomethine)s with highly organized macromolecular architectures with controlled head-to-tail structure. Unlike many condensation polymers that can be made from a bifunctional monomer, very few AB-type poly(azomethine)s are known and well characterized mainly due to the ease of self-condensation between the aldehyde and amine groups.[9] The aza-Wittig reaction,[10] which is the reaction of phosphazenes—obtainable by the Staudinger reaction from organic azides and phosphorus(III) reagents—with carbonyl compounds, has become one of the most efficient methods for the creation of the imine group under mild reaction conditions. In our previous work, we discovered that 1,4-diazidobenzene and terephthalaldehyde derivative readily underwent A_2B_2-type polycondensation reaction (aza-Wittig polymerization) only in the presence of suitable phosphorus(III) reagents, resulting in the corresponding A_2B_2 poly(azomethine) with high molecular weight.[11] This result prompted us to further examine the aza-Wittig polymerization of AB-type monomers having both aldehyde and azide functionality within single molecules. We herein describe the synthesis, characterization, and properties of fully regioregular, head-to-tail coupled, π-conjugated poly(azomethine)s via aza-Wittig polymerization from an AB monomer system.

Results and Discussion

Monomer Synthesis. Scheme 1 illustrates the synthetic route to **6a**−**d**, AB-type monomers containing both the aldehyde and azide functionality. The synthetic strategy was adapted from a

Scheme 1. Synthetic Route to Monomers 6a−d[a]



[a] Reagents and conditions: (a) HNO_2, NaN_3; (b) $BF_3 \cdot Et_2O$, MeOH, reflux; (c) RX, K_2CO_3, acetone, reflux; (d) DIBAL−H, CH_2Cl_2, −78°C; (e) DMP, CH_2Cl_2, room temperature.

* Corresponding author. E-mail: chujo@chujo.synchem.kyoto-u.ac.jp. Fax: +81-75-383-2605 Telephone: +81-75-383-2604.

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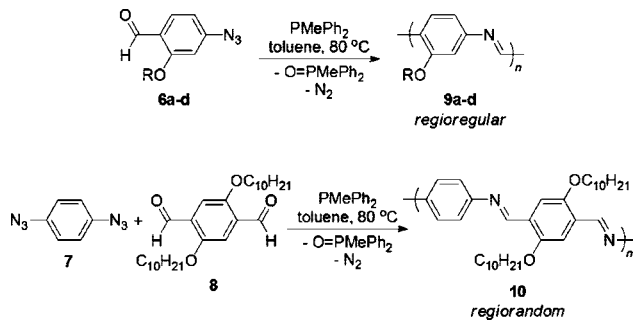
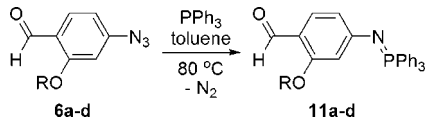
Scheme 2. Synthetic Route to Regioregular (9a−d) and Regiorandom (10) Poly(azomethine)s



Scheme 3. Reaction of 6a−d with PPh_3



procedure previously reported by Myles.[12] The methyl 4-azidosalicylate **3**, which was prepared from 4-aminosalicylic acid **1** according to a literature procedure,[12] was converted into methyl 4-azido-2-alkoxybenzoates **4a−d** by alkylation. Long and/or branched alkyl side chains on the phenyl ring are introduced to improve the polymer solubility because π-conjugated poly(azomethine)s generally have poor solubility in common organic solvents. Treatment of methyl 4-azido-2-alkoxybenzoates **4a−d** with DIBAL−H resulted in the selective reduction of the esters to yield 4-azido-2-alkoxybenzyl alcohols **5a−d**. Oxidation of the free alcohols using a Dess−Martin reagent[13] gave the desired 4-azido-2-alkoxybenzaldehydes **6a−d** in high yields after purification by flash chromatography. The structures of the obtained monomers were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analyses.

Polymer Synthesis. Regioregular poly(azomethine)s **9a−d** were synthesized by adding excess amounts of phosphorus(III) reagents to anhydrous toluene solutions of monomers **6a−d**, respectively, at 80 °C (Scheme 2). In the initial stage of the polymerization, the color of the reaction mixture immediately changed from light yellow to deep orange in addition to the generation of N_2 bubble, indicating the successful progress of the Staudinger reaction. Note that, from the reaction scheme, only the regioregular poly(azomethine)s **9a−d** could be formed. As for a control, a regiorandom poly(azomethine) **10** was synthesized via aza-Wittig polymerization using the diazide **7** and the dialdehyde **8** under similar reaction conditions.[11]

Polymerization with PPh_3. We first tried to use triphenylphosphine (PPh_3), which is one of the most employed reagents in the aza-Wittig reaction, to polymerize AB-type monomers **6a−d** in anhydrous toluene at 80 °C. However, in contrast to our expectation, the polymerization results were rather surprising. In all cases, only the corresponding phosphazenes **11a−d** were obtained in quantitative yields (Scheme 3), whereas no imine group-containing compounds could be obtained. On the other hand, as we previously examined, 1,4-diazidobenzene **7** and terephthalaldehyde derivative **8** underwent A_2B_2-type aza-Wittig polymerization in the presence of PPh_3, which resulted in the corresponding poly(azomethine) with moderate molecular weight (M_n = 2200, PDI = 2.05). This result must come from the difference of the electron density between the resultant phosphazene moieties. In the case of AB-type monomers, the phosphazene and aldehyde groups are connected by a conjugated phenyl moiety to form a "push-and-pull" system. Thus, it is suggested that the electron density of the phosphazene moiety was not enough to proceed AB-type aza-Wittig polymerization. The high stability of the phosphazene enabled us to isolate and characterize the molecular structure even in the presence of atmospheric oxygen and moisture. In addition, the high crystallinity of the phosphazene **11a** derived from monomer **6a** prompted us to further examine a single crystal X-ray diffraction analysis (Figure 1). The crystal structure reveals that not only the low electron density of the phosphazene moiety but also the steric hindrance caused by three phenyl rings are both unfavorable for AB-type aza-Wittig polymerization.

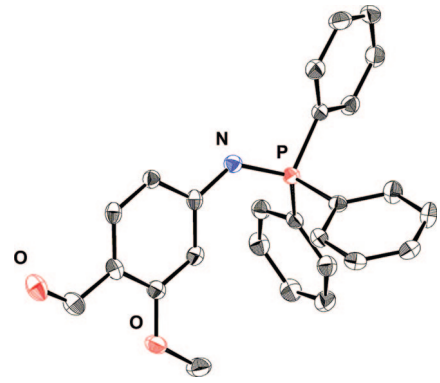


Figure 1. ORTEP drawing of phosphazene **11a** with 50% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 1. Solubilities[a] and Molecular Weights[b] of Synthesized Poly(azomethine)s

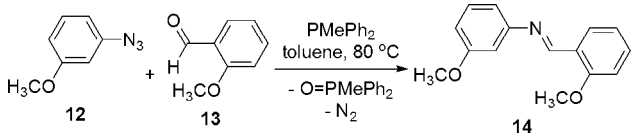
entry	polymer	yield (%)	solubility	M_w	PDI
1	**9a**	93	−	900	1.80
2	**9b**	81	+ −	3800	1.90
3	**9c**	87	+	12000	2.26
4	**9d**	76	+ −	6100	1.85
5	**10**	93	+	133000	2.42

[a] Measured at room temperature in $CHCl_3$. Key: +, fully soluble; + −, partially soluble; −, insoluble. [b] Determined by GPC ($CHCl_3$), polystyrene standards.

Polymerization with $PMePh_2$. We then checked methyldiphenylphosphine ($PMePh_2$) instead of PPh_3 in order to evaluate the electronic effect of phosphines on the aza-Wittig polymerization. It is well-known that the electronic state on phosphorus atom can be varied by modification of the substituents. For example, the electronic density on phosphorus atom of alkyl groups-substituted phosphine is higher than that of triarylphosphine; thus, the reactivity of the aza-Wittig reaction utilizing alkyl groups-substituted phosphine is also predicted to be high. As we expected, $PMePh_2$ displayed much higher activity on the aza-Wittig polymerization, which resulted in the corresponding AB-type poly(azomethine)s **9a−d**. Similarly, as we previously reported, monomers **7** and **8** underwent A_2B_2-type aza-Wittig polymerization in the presence of $PMePh_2$, which resulted in the corresponding poly(azomethine) **10** with high molecular weight.

Polymer Solubility and Molecular Weight. The solubility and molecular weights of the obtained polymers are summarized in Table 1. Regiorandom poly(azomethine) **10** was quite soluble in common organic solvents such as $CHCl_3$, THF, and toluene in spite of its higher degree of polymerization. In contrast, regioregular poly(azomethine)s **9a−d** showed limited solubility. The molecular weights of the obtained polymers were estimated by gel permeation chromatography (GPC) in chloroform at 40 °C, using polystyrene standards for calibration. The regioregular poly(azomethine)s **9a−d** have relatively low molecular weights compared to the regiorandom poly(azomethine) **10**. This could be attributed to the low solubility of regioregular polymers **9a−d** in toluene resulting in termination

Scheme 4. Synthesis of Model Compound 14



of the polymerization, since precipitation of the polymers was observed at a later stage of the reaction.

Polymer Characterization. The molecular structures of the resulting polymers were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. For example, the FT-IR spectra of the polymers **9a**−**d** displayed strong absorption bands at 1560 cm^{-1}, assigned to the azomethine (−CH═N−) stretching. Instead, the strong FT-IR peaks at 2116 cm^{-1} owing to the azide groups in monomers **6a**−**d** completely disappeared in polymers **9a**−**d**. In the ^{1}H NMR spectra, the overall integration ratio between the aliphatic protons and the aromatic protons were consistent with the structures of the polymers. The 100% head-to-tail regioregularity of polymers **9a**−**d** automatically follows from the AB-type nature of the condensation polymerization. The presence of only one nonsplitting peaks around 9 ppm corresponding to the azomethine proton resonances further confirmed the regioregular structures of polymers **9a**−**d**. Moreover, previous reports employing the theoretical study of the aza-Wittig reaction supported the preferential or exclusive formation of (*E*)-imines so that the obtained poly(azomethine)s here would also have the trans conformation.[14]

Electronic Structure. In order to evaluate the electronic structure of the obtained AB-type π-conjugated poly(azomethine)s, model compound **14** was synthesized via aza-Wittig reaction (Scheme 4). Figure 2 shows the UV−vis absorption spectra of the polymer **9c** and the model compound **14** in dilute $CHCl_3$ solution at room temperature. The polymer **9c** exhibited absorption maximum of the longer wavelength at 425 nm and a large red shift of 95 nm relative to the absorption maximum of **14** (λ_{max} = 330 nm) (Figure 2). This result suggests the extension of the π-delocalization length of the polymer **9c** via the AB-type π-conjugated poly(azomethine) backbone.

Properties in the Solid State. In the solid state, regioregular poly(azomethine) **9c** and regiorandom poly(azomethine) **10** display markedly different behavior (Figure 3). Although both absorptions are red-shifted in the solid state relative to the solution spectra, the regioregular analogue (λ_{max} = 465 nm, λ_{edge} = 590 nm) has a greater contribution at higher wavelength than the regiorandom analogue (λ_{max} = 470 nm, λ_{edge} = 560 nm). This result could reflect the elongation of conjugated length and

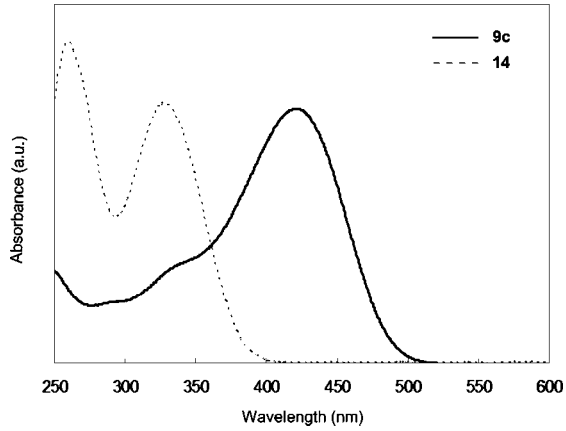


Figure 2. UV−vis absorption spectra of polymer **9c** (solid line) and model compound **14** (dashed line) in dilute $CHCl_3$ solution.

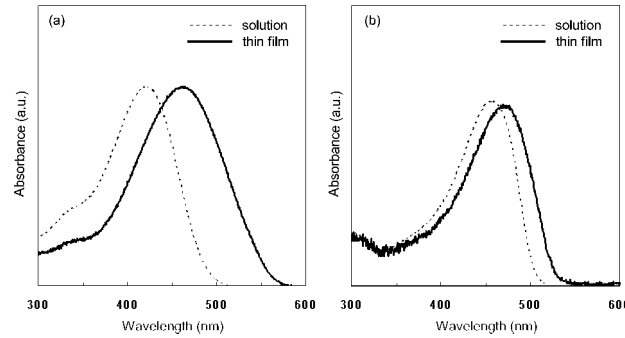


Figure 3. UV−vis absorption spectra of (a) regioregular polymer **9c** and (b) regiorandom polymer **10** in dilute $CHCl_3$ solution (dashed line) and in the solid state (solid line).

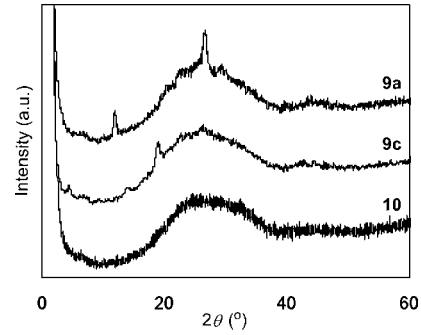


Figure 4. XRD patterns of polymers **9a**, **9c**, and **10**.

better π−π stacking of the polymer chains due to the higher crystallinity of the regioregular polymer **9c** in the film. This type of spectral change is similar to the one observed for highly regioregular PATs upon crystallization.[15] On the other hand, irregular arrangement of the substituents in the regiorandom polymer **10** hampers formation of an ordered assembly, consequently leading to conformational disorder and a decrease in conjugation length.

To further examine the crystallinity of the polymer in the solid state, X-ray diffraction (XRD) measurements were conducted on powder samples of the polymers (Figure 4). The regioregular polymer **9c** has a weak diffraction peak at 2θ of 4.6°, corresponding to an interlayer spacing of 19.2 Å. In contrast, the regiorandom polymer **10** does not show any diffraction peak, indicating the amorphous nature of the material. These results indicate that regioregular analogue forms a layered order structure in which the rigid-rod main chains are separated by the alkyl side chains. In addition, a peak in the diffraction pattern centered at 26.6° for **9a** and 26.4° for **9c** corresponds to a spacing of 3.35 and 3.38 Å, respectively. This side-chain-length independent spacing is assigned to the π−π interchain stacking distance. The above results support the crystalline nature of the regioregular poly(azomethine)s in the solid state.

Conclusions

We have developed AB-type aza-Wittig polymerization for the construction of fully regioregular π-conjugated poly(azomethine)s. The obtained regioregular poly(azomethine)s showed moderate solubility in common organic solvents such as $CHCl_3$, THF, and toluene at room temperature. UV−vis absorption study in dilute $CHCl_3$ solution revealed that the extension of the π-delocalization length of the regioregular poly(azomethine)s via the AB-type π-conjugated poly(azomethine) backbone. In the solid state, UV−vis absorption spectra and XRD data demonstrated that these regioregular poly(azomethine)s have higher crystallinity compared to the regiorandom poly(azome-

thine). The high crystallinity and the solution processability of the polymers could be advantageous for various device applications. Further work is currently underway to apply AB-type aza-Wittig polymerization to the development of novel backbone-containing polymers.

Experimental Section

Materials. Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). Methyl 4-azidosalicylate was synthesized and characterized according to the literature.[12] 1-Azido-3-methoxybenzene was synthesized and characterized according to the literature.[16]

Measurements. ^{1}H and ^{13}C NMR measurements were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz in $CDCl_3$ (0.05% TMS as an internal standard) at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and RI-8020 (TOSOH TSKgel α−3000 column) using $CHCl_3$ as an eluent at 40 °C, after calibration with the standard polystyrene samples. Recyclable preparative high-performance liquid chromatography (HPLC) was performed on a JAI LC-918 using $CHCl_3$ as an eluent. FT-IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Powder X-ray diffraction (XRD) patterns were taken by using Cu Kα radiation with a Shimadzu XRD-600.

General Procedure for Methyl 4-Azido-2-alkoxybenzoates (4a−d). Methyl 4-azidosalicylate (**3**) was synthesized using a modified literature procedure starting from commercially available 4-aminosalicylic acid (**1**).[12] A round-bottomed flask was charged with methyl 4-azidosalicylate and a large excess of the corresponding alkyl halides. To this was added a large excess of anhydrous K_2CO_3, anhydrous acetone solvent, and a stir bar. The reaction was then left to stir overnight in a thermostatic oil bath at 80 °C, after which the solvent was removed via vacuum distillation. Dichloromethane was then added to the residue, and the resulting suspension was filtered to remove excess K_2CO_3 and insoluble byproducts. Afterward, the solvent was removed with a rotary evaporator, and the crude product was chromatographed on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3.

Methyl 4-Azido-2-Methoxybenzoate (4a). The above general procedure was performed with 1.55 g (8.00 mmol) of methyl 4-azidosalicylate, 11.4 g (80.0 mmol) of methyl iodide, 4.15 g (30.0 mmol) of K_2CO_3, and 20 mL of acetone. The crude product was purified by column chromatography with hexane/EtOAc (15/1) to give **4a** (85% yield, 1.41 g).^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, 1 H), 6.63 (d, 1 H), 6.52 (s, 1 H), 3.96 (s, 3 H), 3.86 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.9 (CH_3OOC), 160.2 (C_{Ar}−O), 145.0 (C_{Ar}−N), 133.3 (C_{Ar}−H), 116.5 (C_{Ar}−C), 110.1 (C_{Ar}−H), 103.7 (C_{Ar}−H), 56.2 (CH_3O), 51.7 (CH_3OOC).

Methyl 4-Azido-2-Hexyloxybenzoate (4b). The above general procedure was performed with 1.93 g (10.0 mmol) of methyl 4-azidosalicylate, 4.24 g (20.0 mmol) of hexyl iodide, 4.15 g (30.0 mmol) of K_2CO_3, and 20 mL of acetone. The crude product was purified by column chromatography with hexane/EtOAc (15/1) to give **4b** (78% yield, 2.15 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, 1 H), 6.63 (d, 1 H), 6.52 (s, 1 H), 4.00 (t, 2 H), 3.86 (s, 3 H), 1.83 (m, 2 H), 1.49 (m, 2 H), 1.35 (m, 4 H), 0.91 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.9 (CH_3OOC), 160.2 (C_{Ar}−O), 145.1 (C_{Ar}−N), 133.4 (C_{Ar}−H), 116.5 (C_{Ar}−C), 110.1 (C_{Ar}−H), 103.8 (C_{Ar}−H), 69.0 (CH_2O), 51.7 (CH_3OOC), 32−14 (aliphatic carbons). Anal. Calcd: C 60.63, H 6.91, N 15.15; Found: C 60.89, H 6.91, N 14.87.

Methyl 4-Azido-2-(3′,7′-dimethyloctyloxy)benzoate (4c). The above general procedure was performed with 3.86 g (20.0 mmol) of methyl 4-azidosalicylate, 6.00 g (27.0 mmol) of 1-bromo-3,7-dimethyloctane, 8.29 g (60.0 mmol) of K_2CO_3, and 60 mL of acetone. The crude product was purified by column chromatography with hexane/EtOAc (20/1) to give **4c** (63% yield, 4.20 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, 1 H), 6.65 (d, 1 H), 6.55 (s, 1 H), 4.02 (t, 2 H), 3.85 (s, 3 H), 1.88 (m, 2 H), 1.80−0.80 (br, 17 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.8 (CH_3OOC), 160.1 (C_{Ar}−O), 145.0 (C_{Ar}−N), 133.2 (C_{Ar}−H), 116.4 (C_{Ar}−C), 110.1 (C_{Ar}−H), 103.7 (C_{Ar}−H), 68.8 (CH_2O), 51.7 (CH_3OOC), 40−19 (aliphatic carbons). MS (EI) *m*/*z*: 333.2055 ($C_{18}H_{27}O_3N_3$ requires 333.2052).

Methyl 4-Azido-2-dodecyloxybenzoate (4d). The above general procedure was performed with 1.93 g (10.0 mmol) of methyl 4-azidosalicylate, 5.93 g (20.0 mmol) of dodecyl iodide, 4.15 g (30.0 mmol) of K_2CO_3, and 30 mL of acetone. The crude product was purified by column chromatography with hexane/EtOAc (15/1) to give **4d** (72% yield, 2.61 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, 1 H), 6.60 (d, 1 H), 6.50 (s, 1 H), 3.97 (t, 2 H), 3.85 (s, 3 H), 1.81 (m, 2 H), 1.47 (m, 2 H), 1.40−1.10 (m, 16 H), 0.85 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0 (CH_3OOC), 160.3 (C_{Ar}−O), 145.2 (C_{Ar}−N), 133.5 (C_{Ar}−H), 116.6 (C_{Ar}−C), 110.2 (C_{Ar}−H), 103.9 (C_{Ar}−H), 69.1 (CH_2O), 51.8 (CH_3OOC), 32−14 (aliphatic carbons). Anal. Calcd: C 66.45, H 8.64, N 11.62; Found: C 66.35, H 8.69, N 11.39.

General Procedure for 4-Azido-2-alkoxybenzyl Alcohols (5a−d). A round-bottomed flask was charged with methyl 4-azido-2-alkoxybenzoates dissolving CH_2Cl_2 solution. After cooling down to −78 °C, a large excess of DIBAL-H (1.5 M toluene solution) was added dropwise. The reaction was then left to stir for 1 h at −78 °C, after which the reaction was quenched by adding a large excess of MeOH. After warming up to room temperature, the solution was poured into aqueous potassium sodium tartrate, and the resulting mixture was stirred for 1 h. The mixture was diluted with CH_2Cl_2 and washed with H_2O, and the organic layer was dried over $MgSO_4$. Afterward, the solvent was removed with a rotary evaporator, and the crude product was chromatographed on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3.

4-Azido-2-methoxybenzyl Alcohol (5a). The reaction was carried out by following the procedure described above. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15 (d, 1 H), 6.52 (d, 1 H), 6.37 (s, 1 H), 4.50 (s, 2 H), 3.71 (s, 3 H), 2.63 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.2 (C_{Ar}−O), 140.4 (C_{Ar}−N), 129.5 (C_{Ar}−H), 125.9 (C_{Ar}−C), 110.4 (C_{Ar}−H), 101.6 (C_{Ar}−H), 60.8 (CH_2OH), 55.2 (CH_3O).

4-Azido-2-hexyloxybenzyl alcohol (5b). The reaction was carried out by following the procedure described above. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23 (d, 1 H), 6.60 (d, 1 H), 6.46 (s, 1 H), 4.61 (s, 2 H), 3.94 (t, 2 H), 2.80 (br, 1 H), 1.79 (m, 2 H), 1.46 (m, 2 H), 1.35 (m, 4 H), 0.92 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.6 (C_{Ar}−O), 140.2 (C_{Ar}−N), 129.2 (C_{Ar}−H), 126.0 (C_{Ar}−C), 110.2 (C_{Ar}−H), 102.3 (C_{Ar}−H), 68.0 (CH_2O), 60.9 (CH_2OH), 32−13 (aliphatic carbons). Anal. Calcd: C 62.63, H 7.68; Found: C 62.92, H 7.71.

4-Azido-2-(3′,7′-dimethyloctyloxy)benzyl Alcohol (5c). The reaction was carried out by following the procedure described above. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (d, 1 H), 6.63 (d, 1 H), 6.50 (s, 1 H), 4.64 (s, 2 H), 4.02 (m, 2 H), 1.88 (m, 2 H), 1.80−0.80 (br, 17 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.7 (C_{Ar}−O), 140.3 (C_{Ar}−N), 129.3 (C_{Ar}−H), 126.1 (C_{Ar}−C), 110.3 (C_{Ar}−H), 102.4 (C_{Ar}−H), 68.1 (CH_2O), 61.0 (CH_2OH), 40−20 (aliphatic carbons). MS (EI) *m*/*z*: 305.2107 ($C_{17}H_{27}O_2N_3$ requires 305.2103).

4-Azido-2-dodecyloxybenzyl Alcohol (5d). The reaction was carried out by following the procedure described above. Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25 (d, 1 H), 6.61 (d, 1 H), 6.47 (s, 1 H), 4.63 (s, 2 H), 3.97 (t, 2 H), 2.39 (br, 1 H), 1.80 (m, 2 H), 1.45 (m, 2 H), 1.40−1.10 (m, 16 H), 0.88 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.9 (C_{Ar}−O), 140.5 (C_{Ar}−N), 129.5 (C_{Ar}−H), 126.1 (C_{Ar}−C), 110.4 (C_{Ar}−H), 102.5 (C_{Ar}−H), 68.2 (CH_2O), 61.5 (CH_2OH), 32−14 (aliphatic carbons). Anal. Calcd: C 68.43, H 9.37; Found: C 68.72, H 9.47.

General Procedure for 4-Azido-2-alkoxybenzaldehydes (6a−d). A solution of 4-azido-2-alkoxybenzyl alcohols in CH_2Cl_2 was added to a stirred solution of Dess−Martin periodinane (DMP) in CH_2Cl_2 over 2 min. The solution came to a spontaneous boil for about 5 min. After 1 h, the solution was poured into saturated aqueous $NaHCO_3$ containing $Na_2S_2O_3$, and the resulting mixture was stirred for 30 min. The mixture was diluted with CH_2Cl_2 and washed with H_2O, and the organic layer was dried over $MgSO_4$. Afterward, the solvent was removed with a rotary evaporator, and the crude product was chromatographed on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3.

4-Azido-2-methoxybenzaldehyde (6a). The reaction was carried out by following the procedure described above. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.31 (s, 1 H), 7.84 (d, 1 H), 6.71 (d, 1 H), 6.55 (s, 1 H), 3.92 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.1 (*C*HO), 163.0 (C_{Ar}−O), 147.6 (C_{Ar}−N), 130.2 (C_{Ar}−H), 121.8 (C_{Ar}−C), 111.1 (C_{Ar}−H), 102.3 (C_{Ar}−H), 55.7 (*C*H_3O). MS (EI) *m*/*z*: 177.0537 ($C_8H_7O_2N_3$ requires 177.0538). Anal. Calcd: C 54.24, H 3.98, N 23.72, O 18.06; Found: C 54.50, H 4.16, N 23.48, O 18.32.

4-Azido-2-hexyloxybenzaldehyde (6b). The reaction was carried out by following the procedure described above. Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.37 (s, 1 H), 7.81 (d, 1 H), 6.66 (d, 1 H), 6.52 (s, 1 H), 4.04 (t, 2 H), 1.84 (m, 2 H), 1.49 (m, 2 H), 1.36 (m, 4 H), 0.91 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.0 (*C*HO), 162.6 (C_{Ar}−O), 147.4 (C_{Ar}−N), 129.7 (C_{Ar}−H), 121.8 (C_{Ar}−C), 110.8 (C_{Ar}−H), 102.9 (C_{Ar}−H), 68.6 (*C*H_2O), 32−13 (aliphatic carbons). MS (EI) *m*/*z*: 247.1320 ($C_{13}H_{17}O_2N_3$ requires 247.1321). Anal. Calcd: C 63.14, H 6.93, N 16.99, O 12.94; Found: C 62.87, H 6.99, N 16.83, O 13.24.

4-Azido-2-(3′,7′-dimethyloctyloxy)benzaldehyde (6c). The reaction was carried out by following the procedure described above. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.37 (s, 1 H), 7.84 (d, 1 H), 6.69 (d, 1 H), 6.54 (s, 1 H), 4.09 (t, 2 H), 1.89 (m, 2 H), 1.80−0.80 (br, 17 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3 (*C*HO), 162.8 (C_{Ar}−O), 147.6 (C_{Ar}−N), 130.1 (C_{Ar}−H), 122.0 (C_{Ar}−C), 111.0 (C_{Ar}−H), 103.1 (C_{Ar}−H), 67.2 (*C*H_2O), 40−19 (aliphatic carbons). MS (EI) *m*/*z*: 303.1949 ($C_{17}H_{25}O_2N_3$ requires 303.1947). Anal. Calcd: C 67.30, H 8.31, N 13.85; Found: C 67.43, H 8.39, N 13.56.

4-Azido-2-dodecyloxybenzaldehyde (6d). The reaction was carried out by following the procedure described above. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.39 (s, 1 H), 7.85 (d, 1 H), 6.70 (d, 1 H), 6.54 (s, 1 H), 4.05 (t, 2 H), 1.85 (m, 2 H), 1.48 (m, 2 H), 1.40−1.10 (m, 16 H), 0.88 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3 (*C*HO), 162.7 (C_{Ar}−O), 147.6 (C_{Ar}−N), 130.0 (C_{Ar}−H), 122.0 (C_{Ar}−C), 111.0 (C_{Ar}−H), 103.0 (C_{Ar}−H), 68.8 (*C*H_2O), 32−14 (aliphatic carbons). MS (EI) *m*/*z*: 331.2264 ($C_{19}H_{29}O_2N_3$ requires 331.2260). Anal. Calcd: C 68.85, H 8.82, N 12.68, O 9.65; Found: C 68.93, H 8.65, N 12.59, O 9.79.

Polymerization Procedure. A general polymerization procedure is as follows. In a round-bottom flask were placed a monomer, dry toluene (200 mM), and an excess amount of phosphine at room temperature. The reaction mixture was thoroughly deoxygenated, filled with high-purity argon, and placed in a thermostatic oil bath at 80 °C for 36 h. After cooling down, the reaction mixture was concentrated. Exhaustive extraction of the resulting solid with methanol (Soxhlet extraction) afforded the target polymer. **9a:** IR (ν, cm^{-1}): 1558 (−CH═N−). **9b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.94 (br, 1 H), 8.16 (br, 1 H), 6.81 (br, 2 H), 4.12 (br, 2 H), 1.86 (br, 2 H), 1.40 (br, 2 H), 1.36 (br, 4 H), 0.91 (br, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.1 (*N* = *C*H), 158.0 (C_{Ar}−O), 157.0 (C_{Ar}−N), 128.5 (C_{Ar}−H), 121.7 (C_{Ar}−C), 113.0 (C_{Ar}−H), 105.9 (C_{Ar}−H), 68.6 (*C*H_2O), 32−14 (aliphatic carbons). IR (ν, cm^{-1}): 1559 (−CH═N−). **9c:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.94 (br, 1 H), 8.17 (br, 1 H), 6.85 (br, 2 H), 4.15 (br, 2 H), 1.90 (br, 2 H), 1.80−0.80 (br, 17 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.1 (*N* = *C*H), 158.0 (C_{Ar}−O), 157.0 (C_{Ar}−N), 128.6 (C_{Ar}−H), 121.6 (C_{Ar}−C), 112.9 (C_{Ar}−H), 105.9 (C_{Ar}−H), 70.0 (*C*H_2O), 40−19 (aliphatic carbons). IR (ν, cm^{-1}): 1558 (−CH═N−). **9d:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.94 (br, 1 H), 8.17 (br, 1 H), 6.82 (br, 2 H), 4.12 (br, 2 H), 1.85 (br, 2 H), 1.50 (br, 2 H), 1.40−1.10 (br, 16 H), 0.87 (br, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.1 (*N*═*C*H), 158.0 (C_{Ar}−O), 156.9 (C_{Ar}−N), 128.7 (C_{Ar}−H), 121.6 (C_{Ar}−C), 112.9 (C_{Ar}−H), 105.9 (C_{Ar}−H), 68.5 (*C*H_2O), 32−14 (aliphatic carbons). IR (ν, cm^{-1}): 1558 (−CH═N−).

Characterization of Phosphazene 11a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.10 (s, 1 H), 7.85−7.40 (m, 16 H), 6.35 (s, 1 H), 6.27 (d, 1 H), 3.67 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.7 (*C*HO), 163.4 (C_{Ar}−O), 161.0 (C_{Ar}−N), 132.6−105.3 (aromatic carbons, overlapping), 55.0 (*C*H_3O). MS (EI) *m*/*z*: 411.1389 ($C_{26}H_{22}O_2NP$ requires 411.1388). Anal. Calcd: C 75.90, H 5.39, N 3.40, P 7.53; Found: C 75.66, H 5.63, N 3.37, P 7.47.

Synthesis of Model Compound 14. 1-Azido-3-methoxybenzene (**12**) was synthesized and characterized according to the literature.[16] In a round-bottom flask were placed **12** and 2-methoxybenzaldehyde (**13**), dry toluene, and an excess amount of methyldiphenylphosphine ($PMePh_2$) at room temperature. The reaction mixture was thoroughly deoxygenated, filled with high-purity argon, and placed in a thermostatic oil bath at 80 °C for 24 h. After cooling down, the reaction mixture was concentrated. The crude product was chromatographed on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.92 (s, 1 H), 8.14 (d, 1 H), 7.42 (t, 1 H), 7.28 (t, 1 H), 7.05 (t, 1 H), 6.92 (d, 1 H), 6.78 (m, 3 H), 3.87 (s, 3 H), 3.81 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.2 (*N*═*C*H), 159.5 (C_{Ar}−O), 156.6 (C_{Ar}−O), 154.1 (C_{Ar}−N), 132.7 (C_{Ar}−H), 129.7 (C_{Ar}−H), 127.5 (C_{Ar}−H), 124.5 (C_{Ar}−H), 120.8 (C_{Ar}−H), 113.0 (C_{Ar}−H), 111.4 (C_{Ar}−H), 111.0 (C_{Ar}−H), 106.7 (C_{Ar}−C), 55.5 (*C*H_3O), 55.3 (*C*H_3O). MS (EI) *m*/*z*: 241.1102 ($C_{15}H_{15}O_2N$ requires 241.1103).

References and Notes

(1) (a) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature (London)* **1999**, *401*, 685–688. (b) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197–203. (c) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93–116. (d) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088.

(2) (a) Percec, V.; Zhao, M.; Bae, J.-Y.; Hill, D. H. *Macromolecules* **1996**, *29*, 3727–3735. (b) Grob, M. C.; Feiring, A. E.; Auman, B. C.; Percec, V.; Zhao, M.; Hill, D. H. *Macromolecules* **1996**, *29*, 7284–7293. (c) Liu, Y.; Lahti, P. M.; La, F. *Polymer* **1998**, *39*, 5241–5244. (d) Suzuki, Y.; Hashimoto, K.; Tajima, K. *Macromolecules* **2007**, *40*, 6521–6528. (e) Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214–3221. (f) Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Muellen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571–580. (g) Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030–1034. (h) Nambiar, R. R.; Brizius, G. L.; Collard, D. M. *Adv. Mater.* **2007**, *19*, 1234–1238. (i) Zhu, Y.; Alam, M. M.; Jenekhe, S. A. *Macromolecules* **2002**, *35*, 9844–9846.

(3) (a) Iwan, A.; Sek, D. *Prog. Polym. Sci.* **2008**, *33*, 289–345. (b) Pron, A.; Rannou, P. *Prog. Polym. Sci.* **2001**, *27*, 135–190.

(4) (a) Marvel, C. S.; Hill, W. S. *J. Am. Chem. Soc.* **1950**, *72*, 4819–4820. (b) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878–887.

(5) (a) Fischer, W.; Stelzer, F.; Meghdadi, F.; Leising, G. *Synth. Met.* **1996**, *76*, 201–204. (b) Weaver, M. S.; Bradley, D. D. C. *Synth. Met.* **1996**, *83*, 61–66. (c) Cho, J.-S.; Takanashi, K.; Higuchi, M.; Yamamoto, K. *Synth. Met.* **2005**, *150*, 79–82.

(6) (a) McElvain, J.; Tatsuura, S.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1998**, *95*, 101–105. (b) Di Bella, S.; Fragala, I.; Ledoux, I.; Diaz-Garcia, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 9550–9557. (c) Dutta, P. K.; Jain, P.; Sen, P.; Trivedi, R.; Sen, P. K.; Dutta, J. *Eur. Polym. J.* **2003**, *39*, 1007–1011. (d) Jenekhe, S. A.; Yang, C. J.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1991**, *3*, 985–987.

(7) (a) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729–739. (b) Wojtkowski, P. W. *Macromolecules* **1987**, *20*, 740–748.

(8) (a) Park, S. B.; Kim, H.; Zin, W. C.; Jung, J. C. *Macromolecules* **1993**, *26*, 1627–1632. (b) Yang, C. J.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 1180–1196. (c) Matsumoto, T.; Yamada, F.; Kurosaki, T. *Macromolecules* **1997**, *30*, 3547–3552. (d) Thomas, O.; Inganaes, O.; Andersson, M. R. *Macromolecules* **1998**, *31*, 2676–2678. (e) Destri, S.; Pasini, M.; Pelizzi, C.; Porzio, W.; Predieri, G.; Vignali, C.

Macromolecules **1999**, *32*, 353–360. (f) Nepal, D.; Samal, S.; Geckeler, K. E. *Macromolecules* **2003**, *36*, 3800–3802. (g) Choi, E.-J.; Ahn, J.-C.; Chien, L.-C.; Lee, C.-K.; Zin, W.-C.; Kim, D.-C.; Shin, S.-T. *Macromolecules* **2004**, *37*, 71–78. (h) Liu, Y.; Zhao, Y.-L.; Zhang, H.-Y.; Li, X.-Y.; Liang, P.; Zhang, X.-Z.; Xu, J.-J. *Macromolecules* **2004**, *37*, 6362–6369. (i) Takihana, Y.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2004**, *37*, 7578–7583. (j) Tsai, F.-C.; Chang, C.-C.; Liu, C.-L.; Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **2005**, *38*, 1958–1966. (k) Liu, Y.; Liang, P.; Chen, Y.; Zhang, Y.-M.; Zheng, J.-Y.; Yue, H. *Macromolecules* **2005**, *38*, 9095–9099.

(9) (a) Gauderon, R.; Plummer, J. G. C.; Hilborn, J. G. *Macromolecules* **1998**, *31*, 501–507. (b) Simionescu, C. I.; Grigoras, M.; Cianga, I.; Olaru, N. *Eur. Polym. J.* **1998**, *34*, 891–898. (c) Matsumoto, T.; Matsuoka, T.; Suzuki, Y.; Miyazawa, K.; Kurosaki, T.; Mizukami, T. *Macromol. Symp.* **2003**, *199*, 83–96. (d) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478–5480.

(10) (a) Palacios, F.; Alonso, C.; Aparicio, D.; Rubiales, G.; de los Santos, J. M. *Tetrahedron* **2006**, *63*, 523–575. (b) Brase, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188–5240.

(11) Miyake, J.; Chujo, Y. *Macromolecules* **2008**, *41*, 5671–5673.

(12) Gano, K. W.; Monbouquette, H. G.; Myles, D. C. *Tetrahedron Lett.* **2001**, *42*, 2249–2251.

(13) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.

(14) (a) Cossio, F. P.; Alonso, C.; Lecea, B.; Ayerbe, M.; Rubiales, G.; Palacios, F. *J. Org. Chem.* **2006**, *71*, 2839–2847. (b) Xue, Y.; Kim, C. K. *J. Phys. Chem. A* **2003**, *107*, 7945–7951. (c) Xue, Y.; Xie, D.; Yan, G. *J. Phys. Chem. A* **2002**, *106*, 9053–9058. (d) Lu, W. C.; Liu, C. B.; Sun, C. C. *J. Phys. Chem. A* **1999**, *103*, 1078–1083.

(15) Brown, P. J.; Thomas, D. S.; Kohler, A.; Wilson, J. S.; Kim, J. S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B* **2003**, *67*, 064203.

(16) Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809–1811.

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