Articles

Synthesis and Characterization of Poly(2,6-triptycene)

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ABSTRACT: We report the syntheses of two monomers, 2,6-dibromotriptycene and 2,6-diiodotriptycene, and their applications in the homopolymerization via a nickel(0)-mediated Yamamoto-type polycondensation polymerization, leading to a novel aromatic polymer—poly(2,6-triptycene). This new polymer was characterized by ^{1}H and ^{13}C NMR spectroscopy, which exhibited an excellent match with the NMR spectra of the model compound, 2,2′-bitriptycene. In addition, the polymer was found to be highly soluble in common organic solvents, although it does not contain any flexible side chains. This good solubility was attributed to its high content of triptycene units, whose rigid three-dimensional structure was proposed to prevent dense packing of polymer chains. A highly transparent film could be obtained by spin-casting a chloroform solution. This polymer also demonstrated good thermal stability.

Introduction

Iptycenes are a class of compounds that consist of a number of arene rings joined together to form the bridges of [2.2.2] bicyclic ring systems.[1] The simplest iptycene, triptycene, which contains three benzene rings in a paddlewheel configuration, was first synthesized by Bartlett in 1942.[2] In the past decades, numerous iptycenes have been synthesized and investigated in various fields, including intramolecular charge transfer,[3] astropisomer,[4] and molecular gear devices.[5] These interesting properties are mainly attributed to the unique rigid, three-dimensional structure of iptycenes. Recently, triptycene derivatives have been extensively studied by Chen and Yang to prepare novel supramolecular systems, such as guest−host chemistry[1e,6,7] and molecular cages.[8] In addition, pentiptycene-based crystalline and surface-mounted molecular rotors have been an interesting topic, owing to its rigid and bulky structure.[1e] MacLachlan and coworkers found that pyrazine-containing iptycene derivatives could be applied as shape-persistent ligands for forming unique metal−organic coordination frameworks, which exhibited high thermal stability and reversible solvent adsorption, showing potential as good sorbents for water purification.[9] Our laboratory has previously demonstrated that iptycene derivatives could exhibit high alignment in liquid-crystalline media, owing to their internal free volume.[10]

In addition to small functional molecules, iptycene units have also been attractive building blocks employed to synthesize novel functional polymers.[11−17] Conjugated polymers containing these rigid, three-dimensional itpycene scaffolds have been found to display improved photostability and quantum yields in the solid state[12] as well as enhanced solubility in common organic solvents.[13] These features afforded novel, highly fluorescent conjugated polymers, such as poly(*p*-phenylene-ethynylene)s (PPEs), which have been demonstrated to be ultrasensitive sensory materials for detecting 2,4,6-trinitrotoluene (TNT).[12] In addition, the rigid elaborated scaffolds also introduce additional free volume in the solid-state material, which facilitates rapid analyte diffusion into the polymer film to achieve faster and larger-amplitude responses.[12] This large free volume inherent to the iptycene scaffolds has also been exploited to achieve enhanced liquid crystal alignments of iptycene-containing conjugated polymers.[14] Polymers with high itpycene content were also found to be interesting low-*k* dielectric materials owing to the high degree of internal free volumes.[15] Incorporation of iptycene units into polymers were also found to significantly enhance the polymers' mechanical properties.[16] Additionally, ladder polymers that are solely composed of iptycene units were also synthesized, and this type of polymer demonstrated interesting alignment in polymer matrices.[17] This feature was attributed to the high content of iptycene in the polymer main chain. More interestingly, McKeown and coworkers have recently reported a networked iptycene-type ladder polymer, which exhibited remarkably high hydrogen storage capacity (2.7 wt % at 77 K and 10 bar).[18] This material is one of the most promising polymers of intrinsic microporosity (PIMs) reported for hydrogen storage.[19] PIMs are often rigid and contorted macromolecules, wholly composed of fused ring components, which form microporous organic materials due to their inability to pack efficiently. Their microporosity is independent of their processing history, indicating that the property is intrinsic and arises from the rigid macromolecular structures.[20,22] This is different from traditional microporous polymers that are often formed from extensive cross-linking of solvent swollen polymers. Solvent-processable non-network polymers give robust self-standing films when cast from solution, suitable for use as gas separation membranes.[21] The iptycene center was proposed to provide the site of contortion necessary for solubility and microporosity. In addition to hydrogen storage, PIMs are promising for a wide range of applications including heterogeneous catalysis, membrane separations, and adsorption of organic compounds.[19,22]

In this work, we describe the synthesis of 2,6-dibromotriptycene and 2,6-diiodotriptycene and their applications in the preparation of a novel all iptycene polymer, poly(2,6-triptycene), via a nickel(0)-mediated Yamamoto-type coupling reaction. This polymer was characterized by NMR spectroscopy, differential

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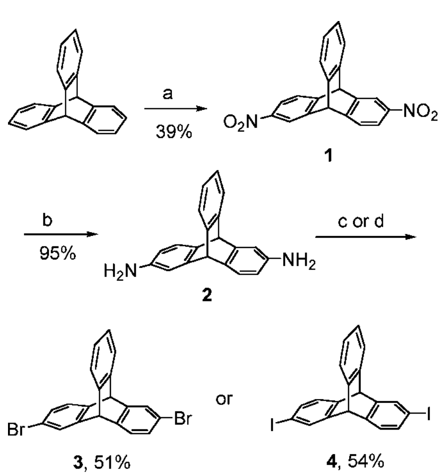
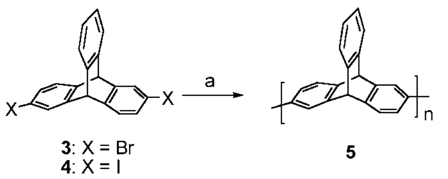
Scheme 1. Synthesis of Monomers 3 and 4[a]



[a] Reagents and conditions: (a) HNO_3 (70%), acetic anhydride, 0 °C to rt; (b) Raney nickel, hydrazine, THF, rt; (c) CuBr, $NaNO_2$, HBr; (d) $NaNO_2$, HCl, KI, H_2O.

Scheme 2. Polymer Synthesis[a]



[a] Reagents and conditions: (a) $Ni(COD)_2$, COD, 2,2′-bipyridyl, DMF, toluene, 85 or 65 °C.

Table 1. Preparation of Polymer 5

monomer	T (°C)[a]	M_n (Da)[b]	yield (%)	PDI[b]	P_n[c]
3	65	5.6K	64	2.0	22
3	85	8.9K	70	1.7	35
4	85	2.4K	71	1.5	10

[a] Reaction temperature. [b] Number-average molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [c] Degree of polymerization (P_n) estimated from M_n.

scanning calorimetry (DSC), thermogravimetric analysis (TGA), and UV−vis absorption spectroscopy. In addition, poly(2,6-triptycene) was found to be completely soluble in common organic solvents, even though it does not contain any flexible side chains.

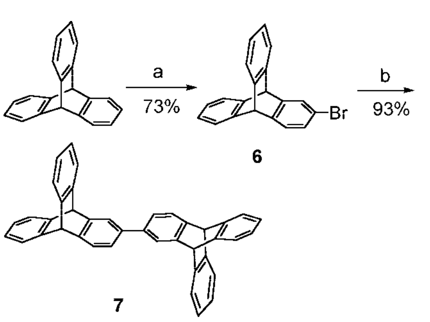
Results and Discussion

Monomer Synthesis. Monomer 2,6-dibromotriptycene (**3**) and 2,6-diiodotriptycene (**4**) were prepared through a Sandmeyer reaction that involves a nucleophilic aromatic substitution of aryl diazonium salt, which can be generated in situ from corresponding arylamines (Scheme 1). Nitration of triptycene with concentrated nitric acid in acetic anhydride led to a mixture of products, with 2,6-dinitrotriptycene (**1**) being the major isomer.[23] The predominant β-nitration was previously attributed to resonance effects, steric factors, and/or strained-ring effects and has been extensively discussed by Klanderman and Perkins.[23d,24] It is worth noting a small amount of 2,7-dinitrotriptycene and trinitrotriptycene could also be isolated.[23] The latter was previously reported to be the major product of a similar reaction with higher reaction temperature and prolonged reaction time.[25] Fortunately, the isolation of compound **1** could be readily achieved via solvent treatment and column chromatography, owing to their difference in solubility and polarity.[9,23] The reduction of dinitrotriptycene to the corresponding diaminotriptycene (**2**) was achieved by using hydrazine and Raney nickel in a high yield.[9,23a,c,25,26] The transformation of amino groups of **2** into bromo and iodo groups was performed according to a procedure developed by Chen and co-workers.[25] The preparation of dibromotriptycene (**3**) was carried out in an aqueous HBr solution using sodium nitrite ($NaNO_2$) and copper(I) bromide (CuBr). Similarly, diiodotritpycene (**4**) was obtained through another Sandmeyer reaction using HCl, $NaNO_2$, and potassium iodide (KI). Both compound **3** and **4** were isolated as a white solid in satisfactory yields, and they could be considered useful building blocks for the preparation of triptycene-containing functional materials. All these compounds have been characterized by NMR spectroscopy and mass spectrometry.

Synthesis of Polymer and Model Compound. With compound **3** or **4** as the monomor, attempts to prepare the target poly(2,6-triptycene) by palladium(0)-catalyzed Stille coupling polymerization using hexamethylditin were not successful. Only small molecular weight oligomers were obtained. The nickel-mediated Yamamoto-type polycondensation reaction (reductive aryl−aryl coupling reaction) of bishalogen monomers, which takes advantage of the fact that only one monomer is needed, has been extensively employed to prepare various conjugated polymers.[27] In this regard, a Yamamoto-type homopolymerization of **3** and **4** was performed using a catalyst system consisting of bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), 2,2′-bipyridyl, and free 1,5-cyclooctadiene (COD) in a toluene/DMF mixture (Scheme 2).[28] It was found that the polymerization of monomer **3** at 65 °C produced a polymer with number-average molecular weight (M_n) of 5.6K (polydispersity index (PDI) = 2.0, 64% yield), which corresponds to 22 repeating units (P_n = 22). Increasing the reaction temperature to 85 °C significantly improved the polymerization, leading to a polymer with M_n of 8.9K (P_n = 35, PDI = 1.7, 70% yield). However, diiodotritpycene **4** exhibited relatively poor polymerization under the same conditions, affording a polymer with M_n of 2.4K at 85 °C (P_n = 10, PDI = 1.5, 71% yield). Table 1 summarizes the polymerization results including yields, M_n, PDI, and P_n. The deviation of PDI from the theoretical value of 2.0 is consistent with other polymers prepared by nickel(0)-catalyzed polymerization, and it may be due to the loss of some lower molecular weight polymer during work-up. In all these cases, polymer **5** was isolated as a white solid, and this polymer was found to be freely soluble in common organic solvents, including tetrahydrofuran, toluene, dichloromethane (CH_2Cl_2), and choroform, although it contains no flexible side chains, which are often used to improve the solubility of polymers. This high solubility may be attributed to the rigid shape persistent structure of triptycene units that prevent dense packing of polymer chains. Our laboratory has previously demonstrated that PPE copolymers with high extent of iptycene units could exhibit excellent solubility in CH_2Cl_2, even for the polymers without any flexible side chains.[29] As a model compound to assist in the structure elucidation of polymer **5**, compound 2,2′-bistriptycene (**7**) was prepared as a spectroscopic reference, and its synthetic route is illustrated in Scheme 3. A treatment of triptycene with bromine at room temperature led to 2-bromotriptycene (**6**) in a reasonable yield.[30] Similar to polymerization of compounds **3** and **4**, a nickel(0)-mediated Yamamoto coupling reaction of **6** afforded the target triptycene dimer **7** as a white solid in a high yield.

Polymer Characterization. The structure of polymer **5** was elucidated by ^1H NMR and ^{13}C NMR spectroscopy. As shown in Figures 1 and 2, both the ^1H and ^{13}C NMR spectra of **5** showed an excellent match with those of the model compound **7**. Definitive peak assignment of the ^1H NMR spectrum of the model compound is easily achieved according to the splitting

Scheme 3. Synthesis of Model Compound 7[a]



[a] Reagents and conditions: (a): Br_2, CH_2Cl_2, rt; (b) $Ni(COD)_2$, COD, 2,2′-bipyridyl, DMF, toluene, 85 °C.

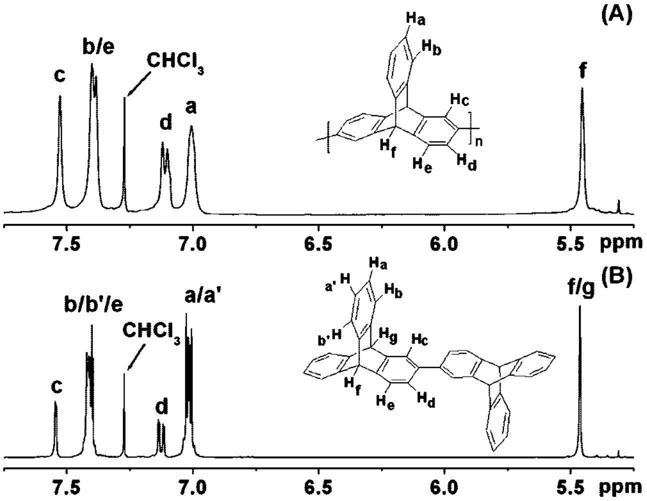


Figure 1. Expanded ^1H NMR spectra of poly(2,6-triptycene) with the inset molecular structure showing the peak assignments (A) and model compound **7** (B).

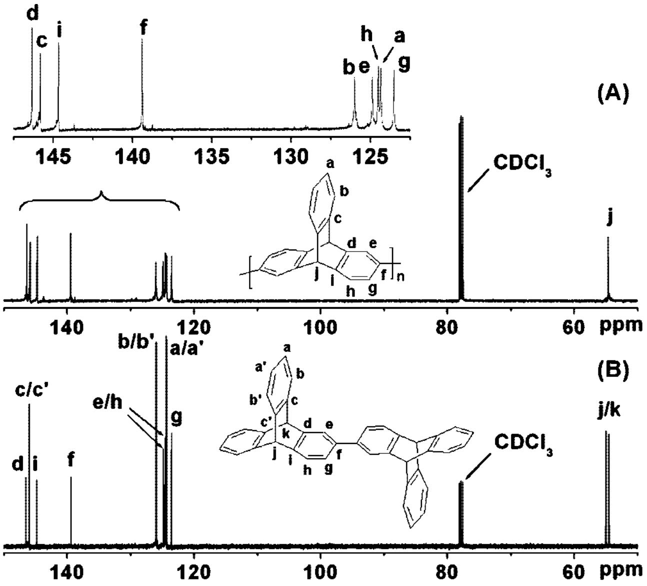


Figure 2. Expanded ^{13}C NMR spectra of poly(2,6-triptycene) with the molecular structure showing the peak assignments (A) and model compound **7** (B).

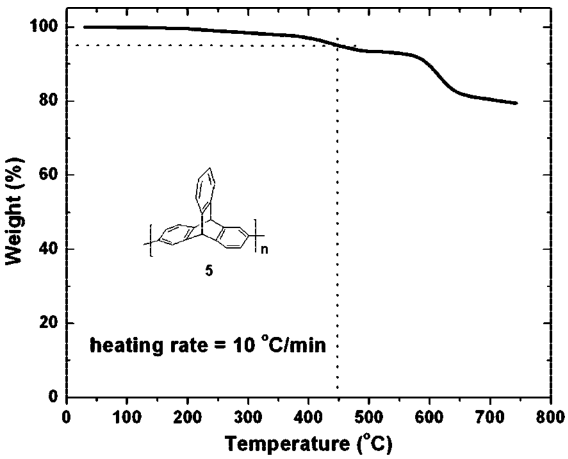


Figure 3. TGA trace of polymer **5** (M_n = 8.9K Da, PDI = 1.7) (10 °C/min under nitrogen).

mode. The doublet at 7.54 ppm and doublet of doublets at 7.11−7.14 ppm are assigned to H_c and H_d, respectively. The signal of H_e was overlapped with the signals of H_b and $H_{b'}$ at 7.39−7.42 ppm, and it is expected to be a doublet with a coupling constant of 7.6 Hz. The doublet of doublets centered at 7.02 ppm are attributed to the signals of H_a and $H_{a'}$, which are not resolved. The characteristic bridgehead protons (H_f and H_g) of model compound were observed at 5.46 ppm, which corresponds to the peak at 5.44 ppm (H_f) of the polymer spectrum. On the basis of this analysis and peak assignment, all the proton peaks of polymer **5** could be assigned accordingly, and they are consistent with the anticipated structure of the repeating unit of polymer **5** (Figure 1 with insets showing molecular structures and detailed peak assignments), indicating the dehalogenation coupling polymerization proceeded as expected. The structure of **5** was verified further by its ^{13}C NMR spectrum (Figure 2A). As in the ^1H NMR spectra, a full peak assignment of the ^{13}C NMR spectrum of polymer **5** (Figure 2A) was made by comparison with the spectrum of model compound **7** (Figure 2B) and estimation of carbon chemical shifts. It was found that the signals of two bridgehead carbons of model compound **7** were clearly resolved, and they were observed at 54.4 and 53.9 ppm (Figure 2B). The corresponding bridgehead carbons of polymer **5** were observed at 54.1 ppm as a single peak.

The thermal properties of polymer **5** were measured by TGA and DSC. As shown by the TGA result (Figure 3 and Figure S1, see Supporting Information), a small mass loss (1−2%) was observed at around 220 °C, and this may be attributed to entrapped solvents. The decomposition of polymer **5** was observed above 420 °C under a nitrogen atmosphere, with a 5% weight loss value at 440 °C. This is consistent with the typical thermal properties of iptycene compounds.[1] DSC studies did not reveal any glass transition temperature in the temperature range of 20−340 °C. This reflects rigid structure of triptycene scaffold.

Figure 4 displays the UV−vis absorption spectra of polymer **5** and model compound **7** in chloroform. The spectra of triptycene and biphenyl in chloroform are also included for comparison (Figure 4). The spectrum of **5** demonstrated an excellent match with that of the model compound, and the spectra of polymer **5** of different molecular weights are identical (Figure S2, see Supporting Information). The absorption band at 240 and 280 nm could be assigned to the absorption of biphenyl unit and triptycene in the polymer chain, respectively, as compared to the spectra of biphenyl and triptycene. However, the shoulder band observed at 290−320 nm for both **5** and **7** was not detected in the spectra of biphenyl and triptycene. This additional absorption band may be attributed to the homoconjugation between the benzo functionalities of triptycene units and the biphenyl units.[31,32] Such homoconjugation was previously observed in the iptycene-containing conjugated polymers[31]

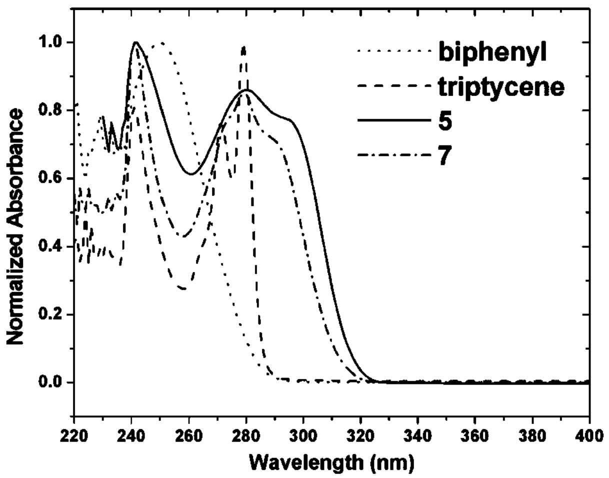


Figure 4. Normalized UV−vis absorption spectra of triptycene, biphenyl, 2,2-bistriptycene (**7**), and polymer **5** (M_n = 8.9K Da, PDI = 1.7) in chloroform.

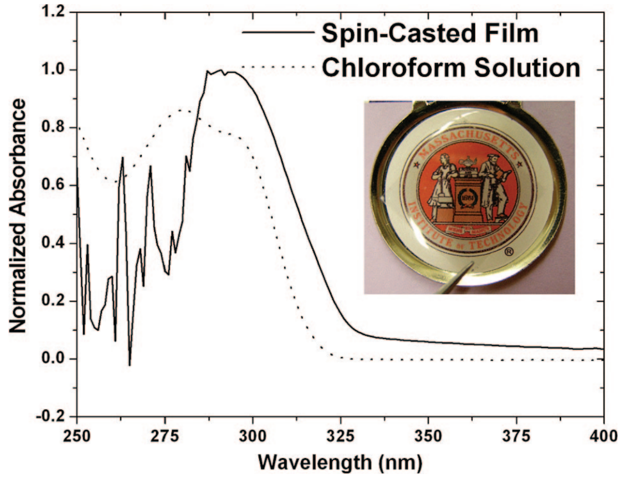


Figure 5. Normalized UV−vis absorption spectra of polymer **5** (M_n = 8.9K Da, PDI = 1.7) in chloroform and at the solid state, with inset showing the image of a spin-cast film on a glass substrate.

and small iptycene molecules.[32] Recently, the design of non-conjugated materials containing π-orbitals close enough to allow energy transfer by Dexter mechanism, which requires a short distance between molecular orbitals involved in the electron/energy transfer for higher rate of energy transfer, has been an interesting topic.[33] A few polymers and oligomers with electron delocalization by aromatic homoconjugation have been reported, such as polymers containing 7,7-diphenylnorbornane segments.[33,34] Similarly, poly(iptycene), which contains high extent of triptycene units, could be a polymer with strong potential for electronic materials. In this regards, compounds **3** and **4** will also be interesting building blocks to prepare novel polymer materials by coupling with other aromatic functionalities.

A clear and colorless film could be easily prepared from spin-cast of a solution of polymer **5** in chloroform. This feature may allow this polymer to be used as membrane for gas separations. Figure 5 displays the UV−vis absorption spectrum of a thin film of **5**, with the inset showing the image of a spin-cast film on a glass substrate. Compared to the absorption spectrum in solution, the film exhibited a single absorption band centered at 292 nm, which is consistent with the shoulder band of spectrum of **5** in chloroform. This indicates that the polymer main chains may adapt a conformation that enhances the aromatic homoconjugation.

Conclusion

A novel aromatic polymer, poly(2,6-triptycene), was synthesized using the well-known nickel(0)-mediated Yamamoto-type dehalogenation polycondensation of 2,6-dibromotriptycene and 2,6-diiodotriptycene, which were prepared from a corresponding nucleophilic aromatic substitution of aryl diazonium salt. This polymer was found to have excellent solubility in common organic solvents, as a result of a high content of triptycene units. It was spin-cast onto a glass plate to give highly transparent homogeneous thin films. It will be interesting to further study this type of polymer, with its strong potential for PIMs for hydrogen storage materials. To further improve the polymerization, it will be attractive to study the polymerization with a cross-linking reagent, such as 2,6,14- and 2,7,14-trihalotriptycene. It will also be interesting to investigate the possibility of preparing triptycene-based dendrimers from the dehalogenation polycondensation of trihalotriptycenes.

Experimental Section

Materials. Triptycene, concentrated nitric acid (HNO_3, 68−70%), acetic anhydride, 1,5-cyclooctadiene (COD), bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$), 2,2′-bipyridyl, hydrazine monohydrate, Raney nickel, copper(I) bromide (CuBr), potassium iodide (KI), sodium bisulfite ($NaHSO_3$), and sodium nitrite ($NaNO_2$) were purchased from Alfa Aesar, Strem Chemical Inc., or Aldrich Chemical Co. and were used without further purification. Anhydrous solvents used in the reactions were purchased from Aldrich Chemical Co. or Mallinckrodt Baker Inc.

General Methods and Instrumentation. All synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Column chromatography was performed using silica gel (40−63 μm) from SiliCycle. NMR spectra were obtained on Bruker Avance 400 MHz or Varian Inova 500 MHz instruments. The ^1H and ^{13}C chemical shifts are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0 ppm and are referenced to residual solvent. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APED II 3T FT-ICR-MS using electron impact ionization (EI) or electrospray ionization (ESI). Melting points were measured on a Mel-Temp II apparatus (Laboratory Devices INC) and were not corrected. Polymer molecular weights were determined on a HP series 1100 GPC system in THF (1 mg/mL sample concentration) at room temperature vs polystyrene standards. TGA was carried out with TA Instruments Q50 under nitrogen at a scan rate of 10 °C/min. Transition temperatures were determined by DSC using a TA Instruments Q1000 DSC at scan rates of 10 °C/min. UV−vis spectra were obtained from Hewlett-Packard 8452A diode array UV−vis spectrophotometer. Fourier transform infrared (FT-IR) spectra were measured on a Perkin-Elmer model 2000 FT-IR spectrophotometer using the Spectrum v. 2.00 software package.

Synthesis of Monomers. *2,6-Dinitrotriptycene* (**1**).[9,23−25] To a solution of triptycene (21 g, 81 mmol) in acetic anhydride (400 mL) cooled by an ice−water bath was added dropwise a concentrated solution of nitric acid (68−70%, 31 mL). After addition, the ice−water bath was removed, and the mixture was allowed to warm to room temperature and stirred at room temperature for an additional 3.5 h. The reaction mixture was poured into water (1.2 L), and the resulting mixture was stirred vigorously overnight. The precipitates were collected by filtration, washed with water, and dried in a vacuum, leading to a slightly yellow solid. This crude product was suspended in benzene (400 mL) and filtered to give a white solid, which was recrystallized from ethyl acetate (9.1 g). The combined filtrates were concentrated on a rotary evaporator. The residue was purified by a column chromatography on silica gel with CH_2Cl_2:hexane (1:1, slowly up to 3:1, v/v), affording the second portion of product (4.6 g, total 13.7 g, 49%). Further purification involved another recrystallization from ethyl acetate; mp >350 °C. ^1H NMR (300 MHz, DMSO-d_6): 8.37 (d, J = 2.4 Hz, 2H), 8.00 (dd, J = 8.1, 2.1 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.54 (dd, $J = 5.4, 3.3$ Hz, 2H), 7.10 (dd, $J = 5.4, 3.3$ Hz, 2H), 6.18 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 151.6, 145.9, 145.2, 142.9, 126.1, 125,0, 124.6, 121.8, 119.1, 51.7. HRMS calcd for $C_{20}H_{12}N_2O_4$ (M^+) 344.0792; found 344.0781.

2,6-Diaminotriptycene (**2**).[9,23a,26] To a solution of 2,6-dinitrotriptycene (0.22 g, 0.64 mmol) in THF (40 mL) was added hydrazine monohydrate (1 mL) and a spatula tip of Raney Ni. The mixture was stirred at 60 °C under Ar for 14 h. After cooling to room temperature, the mixture was filtered through a pad of Celite, and the volatiles were removed in vacuo. The residue was treated with a mixture of CH_2Cl_2/ethyl acetate (1:1), and the resulting white solid was collected by centrifuge and then dried in a vacuum (0.11 g). The supernatant was concentrated and then purified by column chromatography on silica gel with CH_2Cl_2:ethyl acetate (2:1, up to 1:1, v/v), affording a white solid as the second part of the product (0.06 g, total, 0.17 g, 93%); mp 219−221 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6): 7.30 (dd, $J = 5.2, 3.2$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.92 (dd, $J = 5.6, 3.2$ Hz, 2H), 6.62 (d, $J = 2.0$ Hz, 2H), 6.09 (dd, $J = 8.4, 5.6$ Hz, 2H), 5.12 (s, 2H), 4.84 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): 146.9, 146.5, 145.8, 133.0, 124.4, 123.7, 122.9, 110.3, 108.7, 52.2. HRMS calcd for $C_{20}H_{16}N_2$ $[M + H]^+$ 285.1386; found 285.1392.

2,6-Dibromotriptycene (**3**).[25] A mixture of **2** (0.95 g, 3.3 mmol) in HBr (48%, 3 mL) and water (10 mL) was cooled by a salt/ice bath. A solution of $NaNO_2$ (0.62 g, 9.0 mmol) in water (10 mL) was added slowly. After stirring for 30 min, this mixture was added slowly over 35 min to a refluxing mixture of CuBr (1.5 g, 10.4 mmol) in HBr (48%, 5 mL), followed by adding water (20 mL) and HBr (48%, 5 mL) to facilitate the stirring. The resulting reaction mixture was stirred at refluxing for an additional 4 h. After cooling to room temperature, it was extracted with CH_2Cl_2 (100 mL × 2). The organic layers were combined, washed with water, aqueous $NaHSO_3$, and brine in sequence, and dried over anhydrous Na_2SO_4. The solution was concentrated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel with CH_2Cl_2/hexane (1:7, v/v), affording a white solid as the title compound (0.70 g, 51%); mp 254−256 °C. ^{1}H NMR (400 MHz): 7.55 (d, $J = 1.6$ Hz, 2H), 7.40 (dd, $J = 3.2, 5.2$ Hz, 2H), 7.25 (d, $J = 7.6$ Hz, 2H), 7.15 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.05 (dd, $J = 3.2, 5.6$ Hz, 2H), 5.37 (s, 2H). ^{13}C (NMR, 100 MHz): 147.3, 144.2, 143.9, 128.4, 127.2, 125.9, 125.4, 124.1, 119.0, 53.3. FT-IR (KBr) ν/cm^{-1}: 3051, 3017, 2964, 1457, 1402, 1263, 1192, 1162, 1142, 1060, 1021, 916, 866, 800, 752. HRMS calcd for $C_{20}H_{12}Br_2$ (M^+) 409.9300; found 409.9302.

2,6-Diiodotriptycene (**4**).[25] A mixture of 2,6-diaminotriptycene (**2**, 0.60 g, 2.1 mmol), concentrated HCl (5 mL), and water (10 mL) was cooled by an ice−salt bath. A solution of $NaNO_2$ (0.35 g) in water (5 mL) was then added slowly over 10 min. After stirring for an additional 20 min, a solution of KI in water (5 mL) was added dropwise over 30 min. The resulting mixture was allowed to warm to room temperature and then stirred at 80 °C for 3 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (40 mL × 3). The organic layers were combined, washed with saturated $NaHSO_3$ (20 mL × 2), and dried over anhydrous Na_2SO_4. The solution was concentrated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel with CH_2Cl_2/hexane (1:7, v/v), affording a white solid as the title compound (0.58 g, 54%); mp 218−220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, $J = 1.6$ Hz, 2H), 7.39 (dd, $J = 3.2, 5.2$ Hz, 2H), 7. 35 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.04 (dd, $J = 3.2, 5.2$ Hz, 2H). 5.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.4, 144.6, 144.1, 134.5, 132.8, 125.9, 125.8, 124.1, 90.4, 53.2. FT-IR (KBr) ν/cm^{-1}: 3041, 3013, 2968, 1455, 1397, 1262, 1190, 1161, 1143, 1051, 1019, 915, 865, 820, 771, 748. HRMS calcd for $C_{20}H_{12}I_2$ (M^+) 505.9023; found 505.9025.

Polymer Synthesis. *A Typical Synthetic Procedure of Poly(2,6-triptycene)* (**5**). A mixture of compound **3** (0.16 g, 0.39 mmol), Ni(COD)$_2$ (0.17 g, 0.62 mmol), COD (67 mg, 0.62 mmol), 2,2′-bipyridyl (93 mg, 0.62 mmol), anhydrous DMF (2 mL), and anhydrous toluene (6 mL) was stirred at 85 °C under an argon atmosphere for 4 days. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ (100 mL), and the resulting mixture was washed with aqueous HCl solution (4 N), saturated EDTA solution, saturated $NaHCO_3$ solution, and brine in sequence, and dried over anhydrous Na_2SO_4. The solution was concentrated on a rotary evaporator. The solid residue was dissolved in a small amount of $CHCl_3$, and the resulting solution was precipitated in methanol. The solid product was collected by centrifuge. Another precipitation of the product in acetone afforded a white solid as the target polymer (68 mg, 70%). $M_n = 8.9$K Da, PDI = 1.7. ^{1}H NMR (500 MHz): 7.52 (s, 2H), 7.37−7.39 (m, 4H), 7.10 (dd, $J = 1.6, 13$ Hz, 2H), 7.00 (m, br, 2H), 5.44 (s, 2H). ^{13}C (NMR, 500 MHz): 145.8, 145.3, 144.1, 138.9, 125.5, 124,3, 124.0, 123.8, 123.0, 54.1. FT-IR (KBr) ν/cm^{-1}: 3065, 3018, 2954, 1460, 1261, 1184, 1167, 1087, 1021, 874. 823, 743.

Synthesis of Model Compound. *2-Bromotriptycene* (**6**).[29] To a stirred mixture of triptycene (2.3 g, 9.2 mmol), metal iron (18 mg), iodine (12 mg), and CCl_4 (120 mL) was added dropwise a portion of liquid bromine (0.5 mL, 9.7 mmol), and the resulting mixture was stirred at room temperature overnight. This mixture was poured into a saturated Na_2SO_3 solution, and the product was extracted with CH_2Cl_2. The organic layers were combined, washed with saturated Na_2SO_3 solution, water, and brine in sequence, and dried over anhydrous $MgSO_4$. The solution was concentrated on a rotary evaporator, and the remaining white solid residue was subjected to column chromatography on silica gel with CH_2Cl_2/hexane (5:95, v/v), affording a white solid as the title compound (2.3 g, 73%); mp 123−124 °C. ^{1}H NMR (400 MHz): 7.55 (d, $J = 1.6$ Hz, 1H), 7.40 (dd, $J = 3.2, 5.2$ Hz, 4H), 7.26 (d, $J = 7.6$ Hz, 1H), 7.14 (dd, $J = 2.0, 8.0$ Hz, 1H), 7.03 (dd, $J = 3.2, 5.6$ Hz, 4H), 5.42 (s, 1H), 5.41 (s, 1H). ^{13}C (NMR, 100 MHz): 147.8, 145.0, 144.7, 144.6, 128.1, 127.1, 125.6, 125.5, 125.3, 124.0, 123.9, 118.7, 53.9, 53.7. HRMS calcd for $C_{20}H_{13}Br$ (M^+) 332.0195; found 332.0199.

2,2′-Bitriptycene (**7**). A mixture of compound **6** (0.68 g, 2.0 mmol), Ni(COD)$_2$ (0.57 g, 2.1 mmol), COD (0.22 g, 2.0 mmol), 2,2′-bipyridyl (0.21 g, 2.1 mmol), anhydrous DMF (7 mL), and anhydrous toluene (20 mL) was stirred at 85 °C under an argon atmosphere for 2 days. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$ (200 mL), and the resulting mixture was washed with aqueous HCl solution (4 N), saturated EDTA solution, saturated $NaHCO_3$ solution, and brine in sequence, and dried over anhydrous Na_2SO_4. The solution was concentrated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel with CH_2Cl_2/hexane (1:5, slowly up to 1:3, v/v), affording a white solid as the title compound (0.48 g, 93%); mp 287−288 °C. ^{1}H NMR (400 MHz): 7.54 (d, $J = 1.6$ Hz, 2H), 7.39−7.42 (m, 10H), 7.12 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.02 (dd, $J = 3.2, 5.6$ Hz, 8H), 5.42 (s, 1H), 5.46 (s, 1H). ^{13}C (NMR, 125 MHz): 145.9, 145.4, 145.3, 144.2, 138.8, 125.4, 125.3, 124.3, 124.0, 123.8, 123.7, 123.0, 54.4, 53.9. HRMS calcd for $C_{40}H_{26}$ (M^+) 506.2029; found 506.2030. FT-IR (KBr) ν/cm^{-1}: 3038, 3065, 3019, 2922, 2846, 1458, 1190, 1168, 1021, 867, 798, 740.

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Supporting Information Available: TGA results and UV−vis absorption spectra of polymer **5** of different molecular weights, FT-IR spectroscopic data, and NMR spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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