Novel Blue-Light-Emitting Truxene-Containing Hyperbranched and Zigzag Type Copolymers: Synthesis, Optical Properties, and Investigation of Thermal Spectral Stability

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ABSTRACT: Two series of novel alternating polyfluorene copolymers containing 10,15-dihydro-5*H*-diindeno[1,2- α ;1',2'-c]fluorene (truxene) moiety have been prepared through the Pd(0)-catalyzed Suzuki polymerization. The structure and purity of desired polymers is fully characterized by ¹H and ¹³C NMR, UV-vis, and photoluminescent spectroscopy, gel permeation chromatography, elemental analyses, and TGA/DSC. The absorption and PL spectra of all polymers both in solutions and in thin films exhibit similar behaviors. For example, in solutions, the absorption spectra peak at about 360 nm, and the PL spectra show a maximum at about 390 nm with a shoulder at 412 nm. The introducing of the truxene moiety into polyfluorene and the hyperbranched and zigzag type molecular structures significantly reduce aggregation formation and enhance the thermal spectral stability of the desired polymers. They exhibit so of solubility in common organic solvents as well as facile film forming properties. Bright blue emission is observed in both solution and solid states under UV excitation. The investigation of thermal spectral stability reveals that the long-wavelength emission upon thermal treatment usually observed in polyfluorene has been effectively reduced in our polymers.

Introduction

Tremendous progress has been made in the development of organic light-emitting diodes (OLEDs) employing polymers as well as oligomers for their applications in large-area light sources and flexible color displays in the past few decades.¹ OLEDs offer many incomparable advantages, such as good processability, low driving voltage, light weight, fast response, and the possibility of producing displays on flexible substrates.² Highly efficient and stable light emitters with three primary colors (red, green, and blue) are prime criteria for the realization of full color displays. Although all three colors have been demonstrated in OLEDs,^{2b} only red (orange) and green emissions have sufficient efficiencies and lifetimes to be of commercial value.³ Thus, substantial demands for blue light-emitting materials with long-term stability and good color purity still exist. π -Conjugated organic materials with large band gaps, polyfluorenes, ladder-poly-p-phenylenes such as (LPPP)s, and oligofluorenes, are generally regarded as blue-light emitters.^{2,4} However, a prime problem associated with these materials concerns their tendency to form long-wavelength π -aggregates/excimers or ketonic defect sites in solid states during either annealing or passage of current, resulting in poor color purity and hence inhibiting their prospective utilization.^{4c,5}

The general strategies to suppress the red-shifted and less efficient emission are either introduction of bulky side chains, copolymerization with suitable monomers, attachment of sterically demanding end groups, or appending aryl groups onto methylenes.^{4d,h,6} Most of the intensively investigated blue light-emitting materials are linear rigid-rod molecules together with a few exceptions of spiro-linked examples processing a three-

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dimensional (3D) structure.^{4j,k} To provide further insights into the effect of architectures and topologies on polymer properties, we design two novel series of polyfluorene copolymers containing the truxene moiety with either zigzag type (**P1** and **P2**) or hyperbranched skeleton (**P3** and **P4**) (Figure 1).

Truxene has been widely investigated for extensive use as a starting material for the construction of larger polyarenes and bowl-shaped fragment of the fullerenes, liquid crystals, and C_3 tripod materials in asymmetric catalysis and chiral recognition.^{7,8} Few research works on the synthesis and investigation of optical properties of π -conjugated materials based on this heptacyclic polyarene have been reported.⁹ The truxene moiety, by virtue of its unique three-dimensional topology, is an attractive building motif for use as potential dendrimer building block via readily available functionalization at C-2, C-7, and C-12 positions and C-5, C-10, and C-15 positions, respectively.^{9a} Meanwhile, since the power of copolymerization with suitable polyarene derivatives such as anthracene has been demonstrated,^{6c,10} the introduction of the truxene moiety into the polymer backbone might offer some unique properties and substantial improvement. Together with the metalinkage and intrinsic disordered 3D topology, the close face-to-face π -stacking and other interchromophore interactions in solid states are expected to effectively release blue light.

In this paper, we report on the design, synthesis, and characterization of two series of novel alternating polyfluorene copolymers (hyperbranched and zigzag types) containing the truxene moiety (Figure 1). The methylene bridges in both the C-9 position of the fluorene moiety and the C-5, C-10, and C-15 ones of the truxene moiety have been modified with hexyl substituents in order to improve the solubility of the desired polymers as well as to minimize interchain interactions and thus to achieve high photoluminescence (PL) quantum ef-



Figure 1. Structures of polymers P1-P4.

ficiencies. For the syntheses of **P1** and **P2**, one branch of the three-dimensional truxene moiety has been blocked by an aryl group, and the *meta*-linkage in these molecules furnished zigzag copolymers by copolymerization with **M5** in 1:1 molar ration via a Pd(0)-mediated Suzuki coupling reaction. The hyperbranched **P3** and **P4** were obtained by an "A₂ + B₃" approach. The systematic investigation of their thermal spectral stability indicates that the commonly observed red-shifted and less efficient emission in polyfluorenes is efficiently suppressed in our polymers, which makes them good candidates as organic materials for blue-light emitting devices.

Results and Discussion

Synthesis and Characterization. The synthetic route is sketched in Schemes 1 and 2. Fully alkylation has been done by introducing hexahexyl groups on the C-5, C-10 and C-15 positions of readily available truxene afforded **Tr(Hex)**₆ with substantially enhanced solubility. Both the subsequent iodination and bromination proceeded smoothly and afforded the corresponding triiodide M3a and tribromide M3b with excellent yields (90% and 93%, respectively). 4-Methylbenzylboronic acid and 4-methoxybenzylboronic acid were employed to block one branch of the three-dimensional truxene moiety via the Suzuki coupling reaction, during which the boronic acid and the tribromide M3b were in a 1:2 molar ratio. The relatively low yields of M1 and M2 could be attributed to the high reactivity of the boronic acid, which lowered the selectivity and thus produced amounts of di- and trisubstituted byproducts. When one starts from 9,9-dihexyl-2-acetylfluorene, SiCl₄ promoted cyclotrimerization and subsequent alumina-supported $CuBr_2$ bromination afforded the M4 selectively and efficiently.¹⁰ The polymerization of dibromide M1 and M2 with diboronate M5 was carried out with standard Suzuki cross-coupling at a feeding ratio of 1:1, in the

presence of a mixture of toluene and aqueous Na₂CO₃ (2 M) with catalytic amounts (3 mol %) of Pd(PPh₃)₄ under nitrogen atmosphere. **P1** and **P2** exhibited the zigzag figure (Figure 1), in which the *meta*-linkage was introduced by the truxene moiety. Hyperbranched **P3**, however, was synthesized via an "A₂ + B₃" approach. The more reactive triiodide **M3a** resulted in higher molecular weight and better yield compared to its tribromide counterpart. **P4**, in which the terfluorene segments were connected via benzenes by a *meta*-linkage, was also prepared according to the same procedure. The crude polymers were washed with methanol, water, and methanol again, successively, and then were placed in a Soxhlet apparatus and extracted with acetone for 48 h.

All polymers are readily soluble in common organic solvents, such as THF, toluene, chlorobenzene, xylene, etc. The molecular structure of the polymers was verified by ¹H and ¹³C NMR spectroscopy and elemental analysis. The molecular weights of alternating polymers **P1–P4** were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1, the GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index of the polymers are in the ranges (1.0–13.0) × 10⁴ and 1.12–2.04, respectively.

Thermal Stability. The thermal stabilities of P1– P4 were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA), with the results presented in Table 1. All polymers exhibited outstanding thermal stability with onset degradation temperatures (T_d) above 400 °C. The average T_d of our polymers up to 400 °C is similar to that of poly(9,9-dihexylfluorene-2,7-diyl) (PDHF) (ca. 400 °C), suggesting that both the incorporation of truxene moiety and the unique molecular structure (hyperbranched or zigzag) did not affect the thermal stability. The thermally induced

Scheme 1. Synthesis of Monomers M1-M4



Scheme 2. Synthesis of Polymers P1-P4



Table 1. Physical Properties of the Polymers

polymers	$M_{ m n}$	$M_{ m w}$	PD	$T_{\rm d}(^{\circ}{ m C})$
P1	9600	16300	1.70	417
P2	11000	17600	1.60	418
P3a	10580	118800	1.12	421
P3b	9200	18900	2.04	404
P4	129500	15200	1.18	428

phase transition behaviors of the polymers were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Table 2. UV–Vis Absorption and PL Emission Spectral Data of the Polymers in THF and as Films

	solution λ	solution $\lambda_{\max}(nm)$		film λ_{\max} (nm)	
polymers	absorption	emission	absorption	emission	
P1	361	390, 413	354	396, 415	
P2	360	392, 412	355	416	
P3	355	390, 412	358	410, 412	
P4	360	394, 415	355	398, 419	

However, neither the glass transition process (T_g) nor other thermal processes (such as the liquid-crystal phase) which significantly suppressed the mobility of the polymer chain were observed from 20 to 300 °C, indicating the amorphous nature and high branching degree of the polymers.

Optical Properties. The optical properties of the polymers were investigated both in solution and in the solid state. The absorption and emission spectral data are summarized in Table 2. **P1**, **P2**, and **P4** showed almost the same absorption spectra in diluted THF solutions, so Figure 2 illustrates only the absorption spectra of **P4**. The absorption maximum (λ_{max}) peaked at about 360 nm, due to a $\pi - \pi^*$ transition contributed from the conjugated polymer backbone. In comparison



Figure 2. UV-visible and photoluminescence spectra of P1-P4 in THF solutions at room temperature. P1, P2, P3, and P4 exhibit the similar absorption and emission behaviors.



Figure 3. UV-visible and photoluminescence spectra of P1-P4 in film states at room temperature. P1, P2, and P4 exhibit the similar absorption spectra, and P1, P2, and P3 also have similar emission behaviors.

with absorption λ_{max} of the truxene moiety (ca. 310 nm),^{8a} the effective conjugation length in these polymers increased substantially. For P3, we also observed that the absorption maximum slightly blue-shifted 5 nm to 355 nm. Because of the introduction of the *meta*-linkage truxene moiety (P1-P3) or hyperbranched nature (P4), which reduced the conjugative interaction of the polymer backbone and then their effective conjugation length, the PL spectra of our polymers were blue shifted in comparison with polyfluorene (PF) derivatives. All polymers displayed the well-defined vibronic structure in PL spectra. The truxene-functionalized polymers (P1-P3) exhibited the peak at about 390 nm, with a sharp band at ca. 412 nm and a shoulder at ca. 440 nm, while slightly red-shift (ca. 5–10 nm) was observed in those of the hyperbranched polymer **P4** at ca. 394, 415, and 450 nm, respectively. This is attributed to the increase of polymer chain planarity and effective conjugation length upon more release of steric hindrance.

Uniform colorless polymer films were prepared on a quartz glass substrate by spin-coating from solution in toluene or THF (2% w/V) at a spin rate of 2000 rpm. The thickness of all films was about 80-100 nm. All polymers exhibited the very similar absorption behaviors in solid states. The UV-vis absorption maxima of the polymers in thin films appeared at ca. 354 nm, which were slightly blue-shifted from their values in solutions, suggesting that there was little aggregation of the chromophores in solid states. However, the PL spectra of the polymers behaved differently when came from solution to films. The peaks of the zigzag polymers P1 and P2 did not show much bathochromic shift, but

the shoulder peak at ca. 415 nm increased substantially, the intensity of the peak at ca. 396 nm decreased significantly, even disappeared when the solution employed in spin-coating was changed from THF to toluene. The shoulder peak at ca. 445 nm did not exhibit much change in intensity. The PL spectra of a hyperbranched truxene-fluorene copolymer P3 film did not exhibit any change in both the peak position and intensity with respect to those in solutions but only showed less definition of the vibronic structure. By contrast, for P4, it was obvious that the emission spectrum in thin films was much more red-shifted and broader than those of the solution state, with its two emission peaks moving from ca. 394 and 415 nm to ca. 398 and 419 nm, respectively, the shoulder peak of which also increased significantly. It is clear that the intermolecular interactions between neighboring molecules in thin films of P4 were larger than those of truxene-containing polymers. It is also indicative that the incorporating of both the meta-linkage giant truxene moiety and hyperbranched structure is effective to depress the aggregation formation in the solid state.

Thermal Spectral Stability. The color and luminescence stability upon annealing temperatures are critical characters for OLEDs, since the temperature inside the devices could increase depending on the operation conditions. It is well-known that when PF films were heated with exposure to air, an additional broad, featureless band emerged and increased, resulting in a decreased efficiency as well as changing the pure blue emission to an undesirable blue-green color.¹² To examine the thermal stability of our polymers, we



Figure 4. PL emission spectra of **P1**, **P2**, **P3a**, **P3b**, **P4**, and **PDHF** films after thermal annealing at different temperatures and time under air: (a) 100 °C for 3 h; (b) 150 °C for 3 h; (c) 200 °C for 0.5 h; (d) 200 °C for 3 h. During thermal annealing, **P1** exhibits the same behavior as **P2**.

thermally treated the spin-coated polymer films in different manners and then systematically studied their spectra. The commonly reported **PDHF** (polydihexylfuluorene) was employed in our experiment for comparison.

Figure 4 presented the normalized PL emission spectra of our polymers and PDHF films at 100, 150, 200, and 200 °C for 3, 3, 0.5, and 3 h, respectively. Thermal treatment of the PDHF film at 100 °C for 3 h led to a significant increase of the shoulder peak at ca. 460 nm, while the PL spectra of our polymers remained largely intact. With the temperature increased, the additional long wavelength emission at ca. 520 nm became apparent for PDHF, while it was only observed as an insignificant shoulder in PL spectra of P1, P2, and P3b. Any effects were observed on PL spectra of hyperbranched polymer films (P3a and P4) under this condition, indicating that the hyperbranched molecular structure could effectively hamper the aggregation formation of the polymer backbones. The long wavelength emission was further increased for PDHF in Figure 4c, wherein the polymer films were heated to 200 °C for 30 min, but the spectra of our polymers were similar to that in Figure 4b, indicating that an enhanced resistance to the aggregation or keto defect formation in comparison with PDHF exists. When the annealing time was extended to 3 h, a strong green emission at ca. 520 nm dominated in the spectrum of PDHF, those of P3b showed a lower intensity, and those of P1 and P2 were even lower. For the case of P3a and P4, the intensity was significantly reduced. We observed that P1 exhibited the same color stability as P2 due to their almost identical structures.

To better elucidate the interesting thermal spectral behaviors of our polymers, we presented PL spectra in solid states of each polymer before and after thermal annealing at various conditions separately in Figure 5. The tendencies of the PL spectra upon annealing were quite similar for P1 and P2, since both of them contained the zigzag molecular structure as well as moderate molecular weight. P3a exhibited excellent stability; its PL spectrum did not show any measurable spectral change after the annealing either at 150 °C for 3 h or at 200 °C for 30 min. The additional emission band was only characterized as a shoulder after we heated the film at 200 °C for 3 h. In contrast, this band increased steadily with elevated temperatures and prolonged time and became pronounced upon annealing at 200 °C for 3 h. The dependency of aggregation tendency on the molecular weight distribution in linear fluorene homopolymers indicated that a higher molecular weight polymer would possess a lower average chain mobility due to the ability of random coil formation.¹³ So it is reasonable to understand our observations in this manner despite of that our polymers were hyperbranched alternating copolymers. Meantime, the large amount of terminal functional groups in P3b also resulted in decreased thermal stability. Hyperbranched P4 also exhibited outstanding stability; its PL spectrum remained unchanged even after thermal annealing at 200 °C for 3 h, which was similar to the behavior of another hyperbranched polymer.¹⁴ Incorporating the novel truxene moiety substantially improved the emission spectral quality in terms of both narrower spectrum and better thermal stability.



Figure 5. PL emission spectra of polymer films before and after thermal annealing under air: (a) P1; (b) P2; (c) P3a; (d) P3b; (e) P4.

Conclusion

We have synthesized two series of novel conjugated polymers composed of fluorene and truxene units, via the palladium-catalyzed Suzuki coupling reaction. This represents the first synthesis of truxene-containing polymers, which exhibit unique hyperbranched and zigzag type molecular structures. The derived polymers give strong blue both in solutions and in film states. The results from the PL measurements of the annealed films at different temperature and time in the air indicate that the long wavelength emission was significantly reduced and thermal spectral stability was enhanced in our polymers. Hence, we provide a novel approach for preparing blue OLED materials with improved thermal and optoelectronic properties by incorporation of the truxene moiety into the polyfluorene backbones. The performance of single layer OLED devices will be reported elsewhere.

Experimental Section

General Data. Chemicals were purchased from Aldrich, Acros, and Lancaster and used as received. Compounds 10,15dihydro-5*H*-diindeno[1,2- α ;1',2'-*c*]fluorene (truxene),^{7c} **M4**,¹⁰ and **M5**^{5f} were synthesized according to literature procedures. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 200 MHz, Mercury plus 300 MHz, or Bruker 400 MHz using CDCl₃ or CD₂Cl₂ as solovent in all cases. Elemental analyses were carried out on an Elementar Vario EL (Germany). UV– vis spectra were recorded on a Perkin-Elmer Lambda 35 UV– vis spectrometer. PL spectra were carried out on Perkin-Elmer LS 55B Luminescence spectrometer.

General Instrumentation and Conditions for MALDI—TOF MS Spectra. MALDI/TOF (matrix assisted laser desorption ionization/time-of-flight) MS spectra were recorded in Bruker BIFLEX III. MALDI experiments were carried out using a Bruker BIFLEX III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with a N_2 laser emitting at 337 nm (Laser Sciences Inc., Cambridge, MA), a 1-GHz sampling rate digitizer, a pulsed ion extraction source, and an electrostatic reflectron. The laser pulse width was 3 ns, and its maximum power was 200 μ J. Spectra were acquired in the positive-ion mode using the reflectron. The acceleration voltage was 19 kV. The delay voltage was 14.3 kV, the delay time was 200 ns, and the reflectron voltage was 20 kV. Typically, 100 singleshot mass spectra were summed to give a composite spectrum. All data were reprocessed using the Bruker XTOF software. The mass scale was calibrated externally, using the peptides angiotensin II, bovine insulin b-chain, bovine insulin, and equine cytochrome C (Sigma, St. Louis, MO) as mass standards. EI spectral data were obtained using a double-focusing mass spectrometer (ZAB-HS, Micromass, Manchester, U.K.) coupled with a MASPEC II data system. The resolving power (10% valley definition) was typically 1000, and the magnet was scanned at 3 s per decade.

Reagents. MALDI analysis of the polymers utilized Dithranol (DI) purchased from Aldrich (Milwaukee, WI). Inhibitorfree tetrahydrofunan and anhydrous methanol were purchased from Aldrich (Milwaukee, WI). LiCl, NaCl, KCl, RbCl, CsCl, AgTFA, and trifluoroacetic acid (TFA) were purchased from Acros (Fairlawn, NJ).

Sample Preparation. The dendrimers, matrix, and AgTFA were dissolved in THF with concentrations of 1.5×10^{-4} mol/L, 10 g/L, and 1×10^{-2} mol/L, respectively. Alkali salts were dissolved in a mixture solvent (CH₃OH:H₂O:TFA = 2:1:0.03) at 1×10^{-2} mol/L. The mixed sample solution was mixed at the ratio of 1:3:1 (V_{analyte} : V_{matrix} : V_{cation}). We used the dried droplet method to prepare sample target: 1 μ L of sample mixture was applied to the sample target and air-dried.

Tr(Hex)6. With vigorous stirring, 36.5 mL of n-BuLi (1.6 M, 10 equiv) was added to a suspension of truxene (2.00 g, 5.84 mmol) in 60 mL of anhydrous THF at -78 °C and the mixture was kept at this temperature over a period of 2 h. A solution of n-hexyl bromide (8.82 g, 10 equiv) in THF was then added dropwisely. The reaction mixture was allowed to slowly turn to room temperature and stirred overnight. The mixture was then poured into 200 mL of saturated aqueous NaCl solution with stirring for 15 min. The water phase was exacted with ethyl acetate for twice, and then the combined organic phase was dried over MgSO₄. After the solvent was removed, the residue was purified by flash column chromatography using petroleum ether as eluent to afford $Tr(Hex)_6$ (4.95 g, 100%) as a light yellow solid. ¹H NMR (CDCl₃, 300 MHz, ppm, δ): 8.30-8.42 (3H, d, J = 8.1 Hz, Tr-H), 7.45-7.49 (3H, m, Tr-H), 7.31-7.43 (6H, m, Tr-H), 2.83-3.06 (6H, m, CH₂), 1.96-2.18 (6H, m, CH₂), 0.66-1.00 (36H, m, CH₂), 0.54-0.61 (18H, m, CH_3), 0.39–0.51 (12H, m, CH_2). $^{13}\mathrm{C}$ NMR (CDCl_3, 125 MHz, ppm, δ): 153.60, 144.82, 140.30, 138.28, 126.34, 125.87, 124.59, 122.13, 55.56, 36.89, 31.49, 29.54, 23.88, 22.34, 13.86

M3a. A mixture of Tr(Hex)₆ (5.00 g, 5.91 mmol) and 15 mL of solvent (CH₃COOH:H₂SO₄:H₂O = 100:40:3) was heated to 60 °C with vigorous stirring, followed by adding 3 mL of CHCl₃, KIO_4 (1.15 g, 4.9 mmol), and I_2 (2.50 g, 9.85 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere. After the mixture was cooled to room temperature and 150 mL of water was added, the brown precipitate was filtered and purified by recrystallization three times from ethanol to afford M3a (6.51 g, 90%) as a white solid. ¹H NMR (CDCl₃, 300 MHz, ppm, δ): 7.92–8.14 (3H, d, J = 12 Hz, Tr–H), 7.72–7.80 (3H, s, Tr-H), 7.64-7.72 (3H, d, J = 12 Hz, Tr-H), 2.72-2.98 (6H, m, CH₂), 1.88-2.16 (6H, m, CH₂), 0.76-1.08 (36H, m, CH₂), 0.59-0.76 (18H, t, J = 9.0 Hz, CH₃), 0.29-0.58 (12H, m, CH₂). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 155.97, 145.00, 139.54, 137.63, 135.31, 131.53, 126.25, 92.62, 55.95, 36.77, 31.44, 29.37, 23.89, 22.27, 13.88.

M3b. To a mixture of $Tr(Hex)_6$ (10.00 g, 11.81 mmol) and 20 mg of anhydrous FeCl₃ as catalyst in 60 mL of chloroform was added dropwise a solution of bromine (2.05 mL, 40.00 mmol) in 10 mL of chloroform at 0 °C over 1 h. After 24 h, the mixture was washed with saturated sodium thiosulfate solution and brine to remove excess bromine. The precipitate was filtered and washed with water three times. The organic phase was washed with brine. Removal of the solvents gave a yellow

residue, which was then combined with the white precipitate. Recrystallization of the combined solid from EtOH afforded pure **M3b** (11.91 g, 93%) as a white solid. ¹H NMR (CDCl₃, 400 MHz, ppm, δ): 8.15–8.26 (3H, d, J = 8.5 Hz, Tr–H), 7.57–7.65 (3H, s, Tr–H), 7.50–7.57 (3H, d, J = 8.5 Hz, Tr–H), 2.78–2.96 (6H, m, CH₂), 1.96–2.13 (6H, m, CH₂), 0.79–1.03 (36H, m, CH₂), 0.60–0.70 (18H, t, J = 7.2 Hz, CH₃), 0.38–0.57 (12H, m, CH₂). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 156.28, 145.31, 139.26, 138.06, 129.77, 126.29, 125.94, 121.44, 56.39, 37.22, 31.82, 29.74, 24.27, 22.62, 14.21.

M1. To a degassed mixture of Pd(PPh₃)₄ (100 mg, 0.09 mmol) and compound M3b (10.00 g, 9.22 mmol) in 90 mL of THF were added 4-methylbenzylboronic acid (0.627 g, 4.61 mmol) and 60 mL of 2 M Na₂CO₃ aqueous solution. The mixture was refluxed overnight, poured into a saturated solution of ammonium chloride, and extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over MgSO₄. After the solvent was removed by rotary evaporation, the remaining oil was purified by flash chromatography using petroleum ether as eluent to give M1 (1.21 g, 24%) as a light yellow solid. ¹H NMR (CDCl₃, 300 MHz, ppm, δ): 8.32–8.38 (1H, d, J = 8.4 Hz, Tr-H), 8.21-8.26 (1H, d, J = 8.7 Hz, Tr-H)H), 8.15-8.21 (1H, d, J = 8.1 Hz, Tr-H), 7.60-7.69 (4H, m, Ar-H), 7.55-7.60 (2H, dd, J = 4.8 Hz, J = 1.8 Hz, Tr-H), 7.47-7.54 (2H, td, J = 6.3 Hz, J = 2.1 Hz, Tr-H), 7.28-7.36(2H, d, J = 7.8 Hz, Ph-H), 2.80-3.08 (6H, m, CH₂), 2.44-2.46 (3H, s, Ph-CH₃), 1.96-2.18 (6H, m, CH₂), 0.74-1.02 (36H, m, CH₂), 0.56-0.67 (18H, m, CH₃), 0.42-0.56 (12H, m, CH₂). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ):156.08, 155.93, 154.11, 144.36, 139.41, 139.21, 139.13, 138.83, 138.35, 137.11, 129.58, 129.30, 129.27, 126.96, 126.00, 125.55, 125.06, 124.84, $120.87,\,120.85,\,120.49,\,56.07,\,55.95,\,55.80,\,37.06,\,36.91,\,36.84,$ 31.47, 31.44, 29.46, 29.41, 23.94, 23.91, 23.90, 22.29, 22.27, 22.21, 21.17, 13.88, 13.85. MALDI/TOF MS: calcd for C₇₀H₉₄- Br_2 , 1194.6; found, 1094.6 ([M]⁺, 100%).

M2. Compound M2 was prepared according to the procedure described for M1 except that 4-methoxybenzylboronic acid (0.701 g, 4.61 mmol) was used instead of 4-methylbenzylboronic acid. The compound M2 (2.00 g, 39%) was afforded as light yellow solids. ¹H NMR (CDCl₃, 300 MHz, ppm, δ): 8.30– 8.38 (1H, d, J = 8.4 Hz, Tr-H), 8.21-8.35 (1H, d, J = 8.7 Hz, Tr-H), 8.15-8.21 (1H, d, J = 8.7 Hz, Tr-H), 7.65-7.74 (2H, d, J = 8.7 Hz, Ph–H), 7.59–7.64 (2H, s, Tr–H), 7.56–7.60 (2H, dd, J = 4.5 Hz, J = 1.8 Hz, Tr-H), 7.48-7.55 (2H, td, J)= 4.5 Hz, J = 8.4 Hz, J = 1.8 Hz, Tr-H), 7.00-7.10 (2H, d, J = 8.4 Hz, Ph-H), 3.80-3.94 (3H, s, OCH₃), 2.74-3.06 (6H, m, CH₂), 1.90-2.21 (6H, m, CH₂), 0.72-1.04 (36H, m, CH₂), 0.54-0.68 (18H, m, CH₃), 0.36-0.56 (12H, m, CH₂). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 159.25, 156.07, 155.93, 144.79, 139.21, 139.13, 139.07, 138.53, 138.43, 133.77, 129.29, 129.26, 128.12, 125.86, 125.54, 125.48, 124.85, 124.82, 120.85, 120.19, 114.33, 56.05, 55.93, 55.78, 55.43, 37.06, 36.91, 36.84, 31.47, 29.46, 29.44, 29.41, 23.94, 23.90, 22.29, 22.27, 22.25, 22.21, 13.87, 13.85. MALDI/TOF MS: calcd for C₇₀H₉₄Br₂O, 1110.6; found, 1110.6 ([M]⁺, 100%).

P1. To a 1:1 (molar ratio) mixture of M1 (1.00 g, 0.913 mmol), M5 (0.459 g, 0.913 mmol), and Pd(PPh₃)₄ (35 mg, 0.03 mmol) was added a degassed mixture of 4 mL of toluene and 2.7 mL of 2 M Na₂CO₃ aqueous solution. The mixture was vigorously stirred at 90 °C for 48 h under the protection of nitrogen. After the mixture was cooled to room temperature, it was poured into a stirred mixture of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water, and methanol, dissolved with THF, and dedoped with N₂H₄ aqueous solution. The catalyst residues were filtered off, and the organic phase was separated. Removal of the solvents gave a white residue, which was further purified by washing with acetone in a Soxhlet apparatus for 48 h to remove oligomers and was dried under reduced pressure at room temperature to afford the P1 (0.62 g, 53%) as a white solid. ¹H NMR (CDCl₃, 400 MHz, ppm, δ): 8.16–8.24 (3H, m, Tr–H), 7.86–7.93 (2H, d, J = 7.8 Hz, $\rm Ph-H),\, 7.76-7.83$ (8H, m, Ar–H), 7.65–7.76 (5H, m, Ar–H), 7.54–7.62 (1H, m, Ar–H), 7.43–7.52 (1H, m, Ar–H), 7.32– 7.38 (2H, d, J = 7.9 Hz, Ph-H), 2.92-3.13 (6H, m, CH₂), 2.442.52 (3H, s, Ph–CH₃), 2.05–2.16 (10H, m, CH₂), 1.04–1.16 (14H, m, CH₂), 0.88–1.09 (36H, m, CH₂), 0.76–0.88 (8H, m, CH₂, CH₃) 0.42–0.64 (30H, m, CH₂, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 154.45, 151.83, 145.15, 140.15, 139.64, 139.47, 139.40, 138.50, 138.20, 138.09, 136.95, 129.55, 128.79, 127.20, 126.94, 126.10, 125.23, 124.95, 121.31, 120.50, 120.05, 55.84, 55.41, 40.58, 37.13, 31.56, 31.51, 31.39, 29.76, 29.60, 29.52, 24.03, 23.89, 22.61, 22.33, 21.17, 14.03, 13.92, 13.81. Anal. Calcd for C₉₅H₁₂₆: C, 89.98; H, 10.02. Found: C, 89.34; H, 9.93.

P2. P2 was prepared according to the procedure described for **P1** except that compound **M2** (1.00 g, 0.900 mmol) was used instead of compound **M1**. **P2** (0.51 g, 44%) was afforded as a white solid.¹H NMR (CDCl₃, 400 MHz, ppm, δ): 8.14–8.23 (3H, m, Tr–H), 7.90–7.94 (2H, d, J = 7.7 Hz, Ph–H), 7.54– 7.80 (13H, m, Ar–H), 7.46–7.53 (1H, m, Ar–H), 6.96–7.03 (2H, d, J = 8.4 Hz, Ph–H), 3.87–3.93 (3H, s, OCH₃), 2.92– 3.16 (6H, m, CH₂), 2.02–2.15 (10H, m, CH₂), 1.06–1.12 (14H, m, CH₂), 0.88–1.09 (38H, m, CH₂), 0.76–0.82 (9H, m, CH₂, CH₃) 0.48–0.65 (30H, m, CH₂, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 159.12, 154.43, 151.81, 145.08, 140.14, 139.63, 139.45, 139.08, 138.69, 138.20, 138.07, 133.93, 128.78, 128.10, 127.19, 126.06, 124.93, 121.29, 120.03, 114.27, 55.82, 55.78, 55.40, 40.56, 37.14, 31.55, 31.50, 31.38, 29.75, 29.59, 29.52, 29.33, 24.02, 23.88, 22.60, 22.32, 14.02, 13.91. Anal. Calcd for C₉₅H₁₂₆O: C, 88.86; H, 9.89. Found: C, 88.49; H, 9.78.

P3a. To a 2:3 (molar ratio) mixture of M3a (1.23 g, 1.00 mmol), M5 (0.75 g, 1.50 mmol), and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) was added a degassed mixture of 4 mL of toluene and 2.7 mL of 2 M Na₂CO₃ aqueous solution. The mixture was vigorously stirred at 90 °C for 48 h under the protection of nitrogen. After the mixture was cooled to room temperature, it was poured into a stirred mixture of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water, and methanol, dissolved with THF, and dedoped with N_2H_4 aqueous solution. The catalyst residues were filtered off, and the organic phase was separated. Removal of the solvents gave a white residue, which was further purified by washing with acetone in a Soxhlet apparatus for 48 h to remove oligomers and was dried under reduced pressure at room temperature to afford the P3a (0.78 g, 59%) as a white solid. ¹H NMR (CDCl₃, 400 MHz, ppm, $\delta){:}\quad 8.18-8.24 \ (3H,\ m,\ Tr-H),\ 7.76-7.92 \ (16H,\ m,\ Ar-H),$ 7.58-7.64 (3H, m, Ar-H), 7.44-7.56 (4H, m, Ar-H), 7.38-7.45 (1H, m, Ar-H), 2.90-3.11 (6H, m, CH₂), 2.02-2.16 (12H, m, CH₂), 1.10-1.22 (20H, m, CH₂), 0.87-1.09 (38H, m, CH₂), $0.70 - 0.87 (16H, m, CH_2, CH_3) 0.44 - 0.66 (36H, m, CH_2, CH_3).$ ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 140.25, 140.13, 140.08, 138.13, 132.25, 132.15, 131.96, 128.78, 128.55, 128.43, 127.55, 127.20, 126.06, 56.01, 55.85, 55.41, 40.51, 31.54, 31.48, 30.92, 29.72, 29.59, 29.52, 29.32, 24.04, 23.93, 23.86, 22.58, 22.32, 13.99, 13.92. Anal. Calcd for C₂₀₁H₂₇₀: C, 89.87; H, 10.13. Found: C, 88.95; H, 9.93.

P3b. All the conditions and procedures were the same as that in **P3a** except that the triiodo compound **M3a** (1.23 g, 1.00 mmol) was replaced by tribromide **M3b** (1.08 g, 1.00 mmol). The desired **P3b** (0.67 g, 51%) was obtained as a yellow solid. 8.18–8.24 (3H, m, Tr–H), 8.11–8.21 (1H, m, Ar–H), 7.65–7.94 (11H, m, Ar–H), 7.48–7.62 (3H, m, Ar–H), 7.28–7.43 (2H, m, Ar–H), 2.92–3.10 (6H, m, CH₂), 2.02–2.42 (11H, m, CH₂), 1.19–1.30 (18H, m, CH₂), 0.89–1.16 (38H, m, CH₂), 0.70–0.87 (12H, m, CH₂, CH₃) 0.42–0.68 (32H, m, CH₂, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 154.39, 151.82, 150.97, 140.15, 140.06, 139.63, 138.13, 128.78, 127.20, 126.09, 125.93, 124.92, 122.91, 121.28, 121.21, 120.51, 120.04, 119.93, 119.72, 56.03, 55.84, 55.40, 55.19, 40.47, 37.07, 36.96, 31.54, 31.49, 29.73, 29.57, 29.51, 23.97, 23.89, 23.78, 22.58, 22.32, 14.00, 13.91. Anal. Calcd for C₂₀₁H₂₇₀: C, 89.87; H, 10.13. Found: C, 88.53; H, 9.96.

P4. P4 was prepared according to the procedure described for **P3a** except that compound **M4** (1.36 g, 0.900 mmol) was used instead of compound **M3a**. The **P4** (0.71 g, 40%) was afforded as a yellow solid. ¹H NMR (CDCl₃, 300 MHz, ppm, δ): 7.68-8.01 (6H, m, Ar-H), 7.26-7.42 (1H, m, Ar-H), 2.01-2.24 (4H, m, CH₂), 1.02-1.18 (12H, m, CH₂), 0.58-1.00 (10H, m, CH₂, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm, δ): 151.92, 151.79, 150.98, 143.00, 140.76, 140.69, 140.47, 140.10, 140.03, 139.93, 128.77, 127.19, 126.39, 126.18, 126.03, 121.84, 121.52, 121.43, 120.06, 119.99, 119.88, 119.71, 55.41, 55.33, 55.24, 55.15, 40.43, 31.46, 29.70, 23.85, 22.56, 14.01. Anal. Calcd for C₂₃₇H₂₉₄: C, 90.57; H, 9.43. Found: C, 89.46; H, 9.21.

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References and Notes

- (a) Handbook of Conducting Polymers, 2nd ed.; Skotheim, T. A., Ed.; Dekker: New York, 1997. (b) Conjugated Conducting Polymers; Kies, H., Ed.; Springer: Berlin, 1992; Vol. 102. (c) Conjugated Polymers; Brědas, J. L., Sylbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (d) Miller, J. S. Adv. Mater. 1993, 5, 671. (e) Roncali, J. Chem. Rev. 1992, 92, 711.
- (2) (a) Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schoo, H. Adv. Mater. 1998, 10, 1340. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew. Chem., Int. Ed. Engl. 1998, 37, 402. (c) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. Nature 1992, 357, 477. (d) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. Nature 1999, 397, 121.
- (3) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. Adv. Mater. 2000, 12, 1737. (b) Ho, P. K. H.; Kim, J.-S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. Nature 2000, 404, 481.
- (4) (a) Yang, Y.; Pei, Q.; Heeger, A. J. J. Appl. Phys. 1996, 79, 934. (b) Marsitzky, D.; Müllen, K. In Advances in Synthetic Metals-Twenty Years of Progress in Science and Technology; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: Amsterdam, 1999; pp 1–97. (c) Scherf, U.; List, E. J. W. Adv. Mater. 2002, 14, 477. (d) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. J. Am. Chem. Soc. 2001, 123, 946. (e) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T. C.; Hawker, J.; Carter, K. R. J. Am. Chem. Soc. 2001, 123, 6965. (f) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. Adv. Mater. 2000, 12, 828. (g) Yu, W.-L.; Cao, Y.; Pei, J.; Huang, W.; Heeger, A. J. Appl. Phys. Lett. 1999, 75, 3271. (h) Wong, K.-T.; Chinen, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C.-H.; Su, Y.-O.; Lee, G.-H.; Peng, S.-M. J. Am. Chem. Soc.. 2002, 124, 11576. (i) Katsis, D.; Geng, Y. H.; Ou, J.-J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. Chem. Mater. 2002, 14, 4332. (j) Geng, Y. H.; Katsis, D.; Culligan, S. W.; Ou, J.-J.; Chen, S. H.; Rothberg, L. J. Chem. Mater. 2002, 14, 463. (k) Geng, Y. H.; Culligan, S. W.; Ou, J.-J.; Chen, S. H.; Rothberg, L. J. Chem. Mater. 2002, 14, 463. (k) Geng, Y. H.; Chem. Mater. 2003, 15, 542.
- (5) (a) Huber, J.; Müllen, K.; Salbeck, J.; Schenk, H.; Scherf, U.; Stehlin, T.; Stern, R. Acta Polym. **1994**, 45, 244. (b) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Sieger, U.; Göbel, E. O.; Müllen, K.; Bässler, H. Chem. Phys. Lett. **1995**, 240, 373. (c) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. Macromolecules **1999**, 32, 5810. (d) Jenekhe, S. A.; Osaheni, J. A. Science **1994**, 265, 765. (e) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. Adv. Funct. Mater. **2003**, 13, 325.
- (6) (a) Klärner, G.; Miller, R. D.; Hawker, C. J. Polym. Prepr. 1998, 1006. (b) Lee, J. I.; Klärner, G.; Chen, J. P.; Scott, J. C.; Miller, R. D. Proc. SPIE 1999, 2, 3623. (c) Klärner, G.; Davey, M. H.; Chen, W.-D.; Scott, J. C.; Miller, R. D. Adv. Mater. 1998, 10, 993.
- (7) (a) Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, L. T. Science 2001, 294, 828. (b) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. Science 2002, 295, 1500. (c) Gómez-Lor, B.; de Frutos, Ó.; Echavarren, A. M. Chem. Commun. 1999, 2431. (d) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. J. Am. Chem. Soc. 1995, 117, 6410. (e) Sygula, A.; Rabideau, P. W. J. Am. Chem. Soc. 2000, 122, 6323. (f) Perova, T. S.; Vij, J. K. Adv. Mater. 1995, 7, 919. (g) Fontes, E.; Heiney, P. A.; Ohba, M.; Haseltine, J. N.; Smith,

A. B. Phys. Rev. A. 1988, 37, 1329. (h) Destrade, C.; Malthete,

- (a) Cao, X.-Y.; Zhang, W.-B.; Wang, J.-L.; Zhou, X.-H.; Lu, H.; Pei, J. J. Am. Chem. Soc. 2003, 125, 12430. (b) Pei, J.;
- (a) 161, 51.5. *An. Chem. Soc.* 2003, 125, 12450. (b) 161, 51, Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. *J. Am. Chem. Soc.* 2003, 125, 9944.
 (9) (a) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* 1999, 32, 361. (b) Marsitzky, D.; Scott, J. C.; Chen, J.-P.; Lee, V. Y.; Miller, R. Marstay, D., Boott, J. C., Ola, J. T., Bee, V. T., Hiller, D.; Setayesh, S.; Müllen, K. Adv. Mater. 2001, 13, 1096.
 (10) Zhou, X.-H.; Yan, J.-C.; Pei, J. Org. Lett. 2003, 5, 3543.
 (11) Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457.

- (12) (a) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. Macromolecules **1998**, 31, 1099. (b) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klaerner, G.; Miller, R. D.; Miller, D. C. Macromolecules 1999, 32, 361. (c) Lee, J.-I.; Klaerner, G.; Miller, R. D. Chem. Mater. 1999, 11, 1083.
 (13) Weinfurtner, K.-H.; Fujikawa, H.; Tokito, S.; Taga, Y. Appl.
- Phys. Lett. 2000, 76, 2502.
- (14) Li, J.; Bo, Z.-S. Macromolecules 2004, 37, 2013.

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