Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 2789–2793 **2789**
DOI: 10.1021/ma902486y

Synthesis of Stair-Stepped Polymers Containing Dibenz[*a*,*h*]anthracene Subunits

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Received November 9, 2009; Revised Manuscript Received February 5, 2010

ABSTRACT: Polycyclic aromatic monomers based on substituted dibenz[*a*,*h*]anthracene frameworks have been prepared in high yields. From these, several fluorescent stair-stepped conjugated polymers containing fused aromatic subunits have been synthesized via Sonogashira polycondensations and Glaser-type oxidative couplings. The new polymers were characterized by NMR spectroscopy, gel-permeation chromatography (GPC), UV−vis, and fluorescence spectroscopy.

Introduction

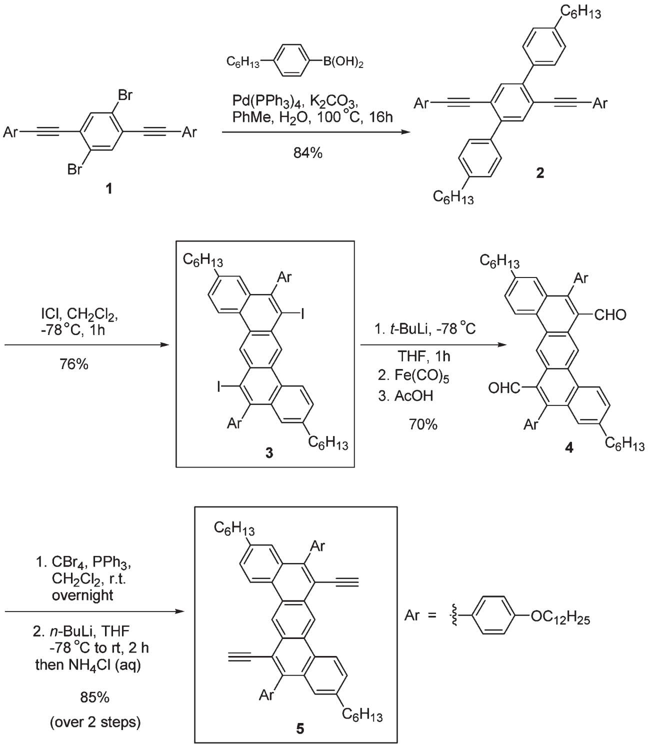
Poly(aryleneethynylene)s (PAEs)[1] represent a class of conjugated polymers that has received much attention over the past two decades due to their interesting electronic and photophysical properties. In general, PAEs are highly fluorescent and relatively photostable. These properties, along with their ease of synthesis, make PAEs a popular class of conjugated polymers that has found numerous technological applications, e.g., in the field of chemical sensors.[2] The general structure of a PAE, i.e., alternating aromatic blocks and carbon−carbon triple bonds, allows for great flexibility in the design and tunability of the polymer's physical properties. Harnessing the power and versatility of organic synthesis, it is possible to prepare diverse monomers containing virtually any degree of structural complexity, which could then be used to synthesize a range of polymers with varying properties. As a result of our recent work on dibenz[*a*,*j*]anthracene-based J-aggregating macrocycles,[3] we became interested in incorporating the isomeric dibenz[*a*,*h*]anthracene motif into conjugated polymers. Over the years, the aryl component of PAEs has seen a wide variety of different aromatic groups, with the simple benzene ring being the most common, i.e., poly(phenyleneethynylene)s (PPEs). Polycyclic aromatic moieties such as anthracene have also been used frequently,[4] and previous work in our group has also employed more complex building blocks such as dibenzochrysene[5] and triphenylene.[6] In most of the aforementioned examples, the resulting polymers can be approximated to linear rigid rods, as a consequence of the *para*-substitution pattern between repeat units of the polymer backbone. With 6,13- and 5,12-linkage patterns on our dibenz[*a*,*h*]anthracene building block, the resulting polymers would adopt a "stair-stepped" structure instead, and we were curious as to how this aromatic moiety, along with the unusual substitution patterns, would affect the physical properties of the resulting polymers.

Herein, we report the synthesis of new monomers containing dibenz[*a*,*h*]anthracene subunits and their successful incorporation into conjugated polymers.

Results and Discussion

The dibenz[*a*,*h*]anthracene-based monomers **3** and **5** were synthesized in good yields from the same dibromide **1** over two and four steps, respectively (Scheme 1). Subjecting dibromide **1** to double Suzuki coupling with 2 equiv of 4-hexylphenylboronic acid under generic conditions led to the terphenyl derivative **2**, which was then converted to monomer **3** via a 2-fold electrophilic cyclization brought about by treatment with iodine monochloride at −78 °C. Diiodide **3** can be converted to monomer **5** over several steps, starting with the formation of dialdehyde **4** via a lithiation/formylation procedure, followed by a Corey−Fuchs homologation[7] to establish two terminal alkynes. Straightforward conversion of diiodide **3** to dialkyne **5** via a Sonogashira coupling/deprotection protocol tends to be unsuccessful, as we have recently described elsewhere.[3]

Scheme 1. Synthesis of Monomers 3 and 5



Diiodide monomer **3** was used in the preparation of polymers **8** and **9** via palladium-catalyzed Sonogashira polycondensation with comonomers **6** and **7**, respectively (Scheme 2). We reacted

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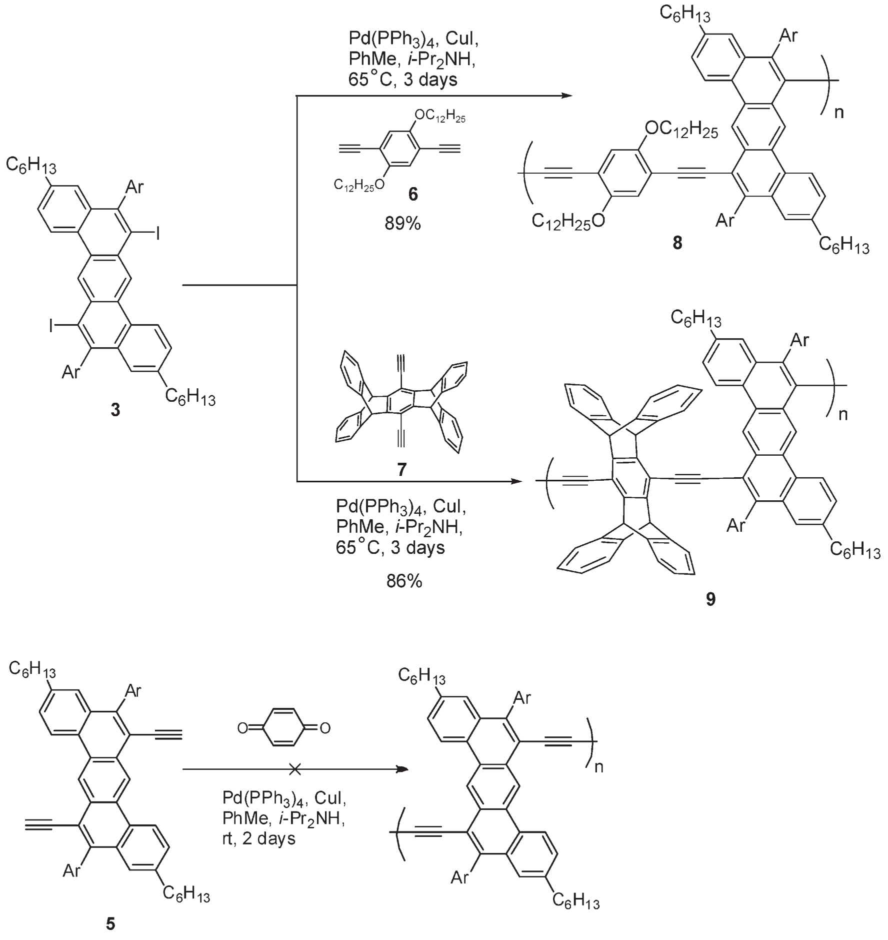
Scheme 2. Synthesis of Polymers 8 and 9

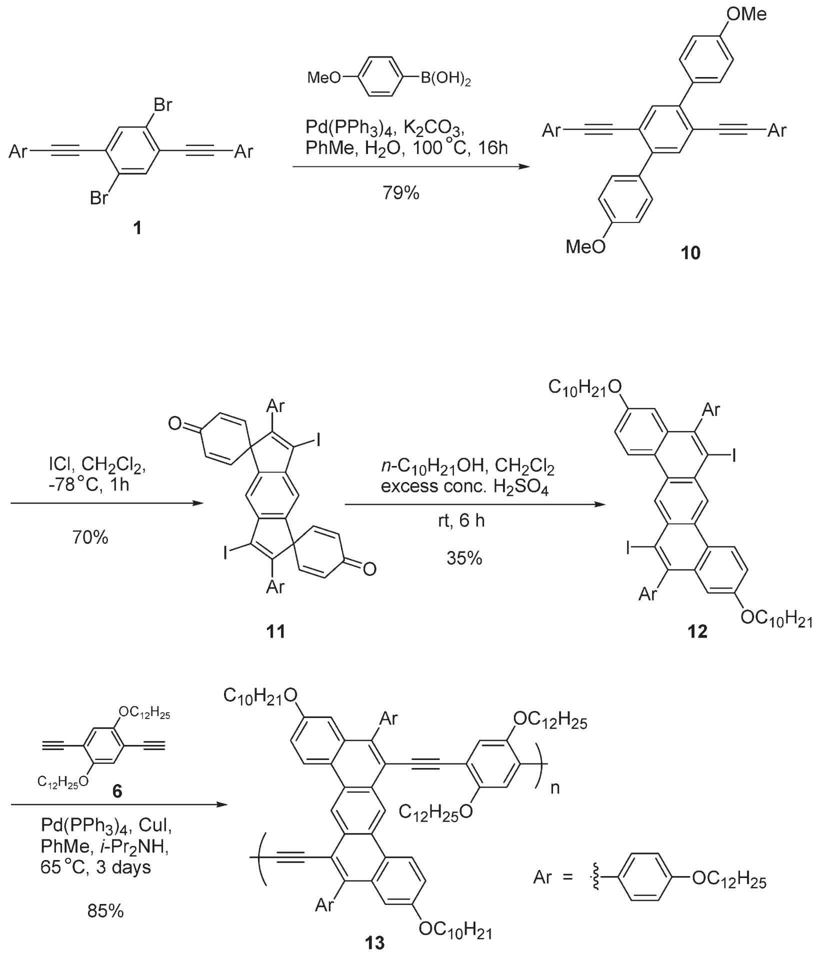


the simple dialkyne **6** with the sterically hindered diiodide **3** in order to test the latter's viability in polymer formation. This turned out to be facile, giving the desired polymer in 89% yield. In the second reaction, the sterically bulky monomer **7** (6,13-diethynylpentiptycene), which had been previously used in the production of nonaggregating poly(arylene ethynylene)s,[8] was successfully copolymerized with **3**. The successful reaction of these two hindered molecules attested to the reactivity and viability of diiodide **3** as a monomer. Gratifyingly, polymers were obtained in high yield in both cases, with **8** being isolated as an orange solid and **9** as a lemon-yellow solid. We also attempted a homopolymerization of monomer **5** using modified Glaser-type coupling conditions with *p*-benzoquinone as the oxidant. Unfortunately, the yield in this case was much lower (ca. 60%), and the purification process also proved challenging. As a result, only a very minute quantity of the butadiyne-type polymer could be isolated, precluding the possibility of rigorous characterization. Furthermore, the polymer was found to have low solubility in various organic solvents. In conclusion, using dialkyne **5** to form a stair-stepped homopolymer appears to be unsuccessful. Based on the above findings, the adequately substituted dibenz[*a,h*]anthracene motif can easily be incorporated into poly(aryleneethynylene)s via Sonogashira polycondensation, but accessing butadiyne-type polymers using Glaser coupling proved to be more problematic.

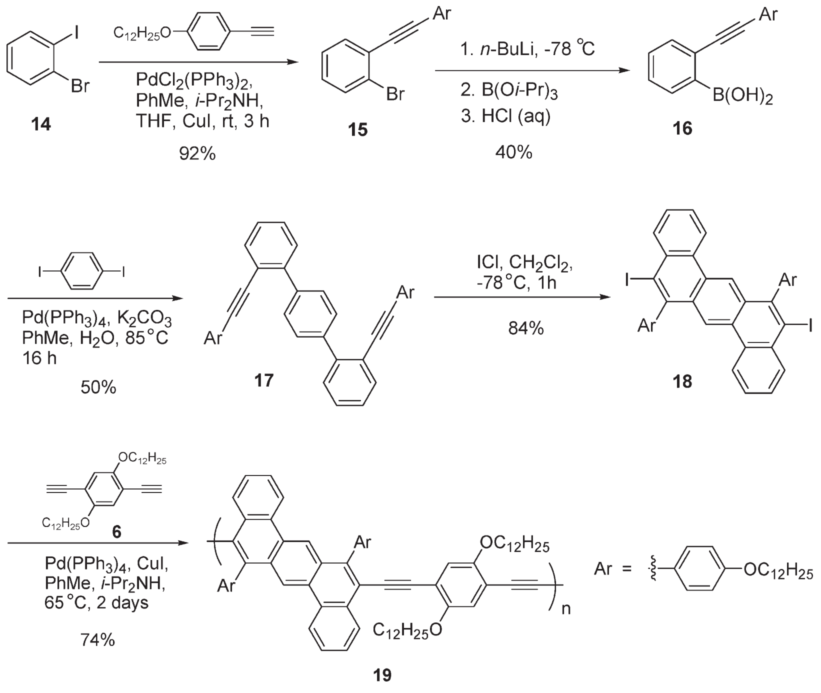
To investigate the effects of alkoxy vs alkyl substitution on the photophysical properties of the resulting polymers, the analogous monomer **12** was synthesized. This diiodide **12** can once again be prepared using a sequence of transformations (Scheme 3) similar to those used in the synthesis of our J-aggregating dibenz[*a,j*]anthracene-based macrocycles. Beginning with dibromide **1**, double Suzuki coupling with 4-methoxyphenylboronic acid affords terphenyl **10** in good yield. The terphenyl is subjected to iodine monochloride to produce the bis-spirocyclic compound **11**, which is partially purified and subsequently converted to the desired diiodide monomer via an acid-catalyzed rearrangement. Using Sonogashira conditions identical to those used in synthesizing polymer **8**, monomer **12** was copolymerized with dialkyne **6** over 3 days to give poly(aryleneethynylene) **13**. The conversion occurred in high yield, and polymer **13** was isolated as a red solid.

Following the successful application of the dibenz[*a,h*]anthracene-based monomers **3** and **12** in Sonogashira polymerization, we then explored other dibenz[*a,h*]anthracenes bearing different substitution patterns. This led to the synthesis of monomer **18**, in which iodine atoms are situated at carbons 5 and 12 of the polycyclic arene instead of carbons 6 and 13, which would produce a structurally different polymer backbone featuring "stair steps" of gentler gradient. The synthesis of polymer **19** (Scheme 4) begins with the commercially available 1-bromo-2-iodobenzene, which is subjected to an iodine-selective Sonogashira coupling to give compound **15**. For unknown reasons, attempts to prepare terphenyl **17** by Suzuki coupling 2 equiv of **15** with benzene-1,4-diboronic acid were unsuccessful. However, when **15** was first converted to boronic acid **16**, followed by Suzuki coupling with $^1/_2$ equiv of 1,4-diiodobenzene, the terphenyl derivative **17** could be obtained in reasonable yield. Subsequent double electrophilic cyclizations with iodine monochloride were carried out on **17** to give the target monomer **18**. The diiodide was then copolymerized with dialkyne **6** to afford polymer **19** (deep red solid) in high yield.

Scheme 3. Synthesis of Polymer 13



Scheme 4. Synthesis of Polymer 19



Polymer **8** shows an absorption maximum ($\lambda_{\max}$) of 436 nm in solution and is a blue-green emitter (Table 1, Figure 1). Its solution photoluminescence spectrum shows peak emission at 450 nm, with a secondary peak at 483 nm. Polymer **9**, which incorporates the bulky pentiptycene unit, displays blue-shifted absorption and emission relative to polymer **8**. The steric bulk of

Table 1. Characterization and Spectroscopic Data for Polymers 8, 9, 13, and 19

polymer	M_n/M_w[a] (10^3 g mol^{-1})	λ_{max} (nm) solution (ε/L mol^{-1} cm^{-1})[b]	λ_{max} (nm) thin film	λ_{em} (nm) solution (thin film)	Φ_f solution[c] (thin film)[d]	lifetimes (bimodal) (ns) solution	lifetimes (bimodal) (ns) thin film
8	21.5/50.2	436 (4200)	447	450 (509)	0.29 (0.050)	1.0 (94%) 2.7 (6%)	1.4 (98%) 5.1 (2%)
9	10.6/25.7	392 (21900)	336	430 (505)	0.34 (0.049)	2.0 (93%) 6.0 (7%)	1.7 (97%) 6.7 (3%)
13	19.0/72.0	448 (26600)	457	457 (550)	0.32 (0.070)	1.4 (97%) 3.5 (3%)	2.0 (95%) 7.4 (5%)
19	10.4/17.4	454 (35300)	450	507 (579)	0.23 (0.018)	1.1 (92%) 2.6 (8%)	1.2 (98%) 4.2 (2%)

[a] Determined by GPC using polystyrene standards. [b] Molar absorptivity based on the molecular weight of a repeating unit. [c] Against quinine sulfate in 0.1 M H_2SO_4 (Φ_f = 0.546, λ_{ex} = 366 nm).[9] [d] Against perylene in PMMA (Φ_f = 0.87, λ_{ex} = 412 nm).[10]

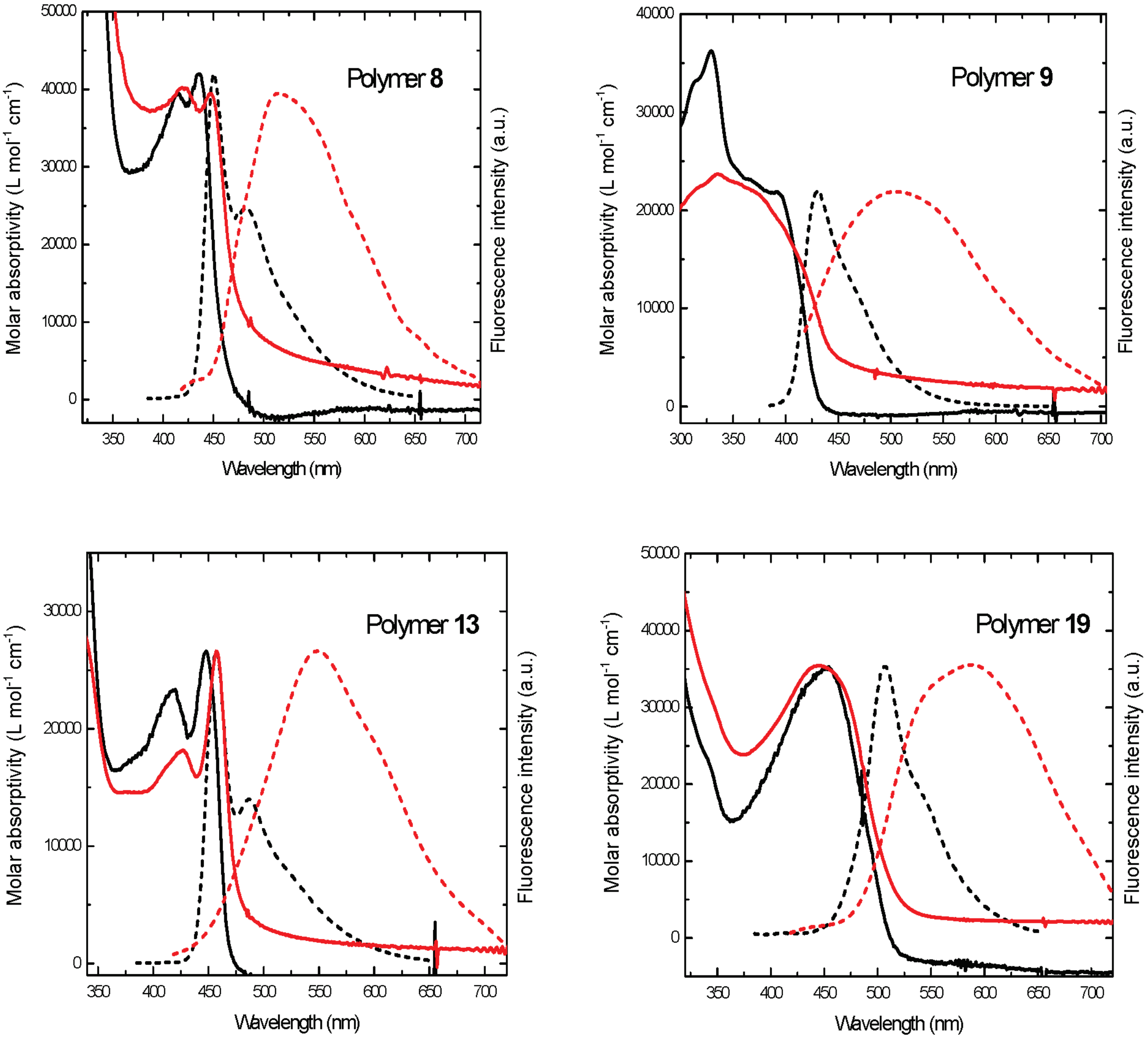


Figure 1. UV–vis (solid lines) and fluorescence (dashed lines) spectra of polymers **8**, **9**, **13**, and **19** in chloroform solution (black) and in thin films (red; normalized).

the pentiptycenes probably reduces overall conjugation along the polymer backbone by twisting the monomer subunits relative to one another. These factors lead to the observation of pure blue emission instead of blue-green. Another interesting feature of polymer **9** is that unlike the pentiptycene-containing PPEs previously synthesized in our group,[11] the presence of that bulky comonomer does not seem to prevent aggregation, as evidenced by the red shift and reduced fluorescence quantum yield of polymer **9** films compared to the corresponding solutions. We believe there are two reasons for this. First, unlike the pentiptycene-containing PPEs, polymer **9** incorporates rather large polycyclic aromatic dibenz[*a*,*h*]anthracene units. By contrast, the much smaller comonomers (single benzene ring) of our pentiptycene-containing PPEs are dwarfed by the larger pentiptycene units, resulting in polymers whose backbones are exceedingly well-shielded sterically, thus preventing aggregation and self-quenching in concentrated solutions and thin films. With such large π-surface areas present in polymer **9**, the three-dimensional bulk of the pentiptycene units are unable to effectively shield the polymer backbone, and as a result, interchain $\pi-\pi$ stacking between polycyclic aromatic units still occurs, producing bathochromic shifts and lowered quantum yields. Second, it must be noted the polymer **9** is structurally a stair-stepped polymer rather than a PPE, whereby the two flanking pentiptycene groups are connected to the dibenz[*a*,*h*]anthracene unit at different "levels" of the "staircase" (vs *para* substitution in PPEs), resulting in further reduction of the pentiptycene shielding efficiency. As for polymer **13**, the replacement of alkyl chains with alkoxy groups (compare with polymer **8**) in the dibenz[*a*,*h*]anthracene subunits brought about a small red shift. Apart from this, the spectral profiles of the structurally similar **8** and **13** are nearly identical. Polymer **19**, which features 5,12-substituted dibenz[*a*,*h*]anthracene repeat units, experiences less intrachain steric repulsions between the monomer repeat units compared to polymer **8**. Thus, increased conjugation and a corresponding bathochromic shift in the absorption and fluorescence spectra were expected. This was indeed observed, making polymer **19** the most spectroscopically red-shifted polymer of the series, showing maximum absorption at 454 nm and green emission at 507 nm (with a shoulder at 541 nm).

Conclusions

Several new polycyclic aromatic monomers based on the dibenz[*a*,*h*]anthracene motif have been synthesized from readily available starting materials. These monomers are easily copolymerized with a variety of comonomers in cross-coupling polymerizations to give fluorescent stair-stepped poly(aryleneethynylene)s. These conjugated polymers exhibit high solubilities as well as relatively blue-shifted absorption and emission maxima. We have found that the degree of blue-shifting can be tuned by employing comonomers of varying steric bulk and also by changing the substitution pattern on the polycyclic aromatic component. These properties suggest potential applications as blue-to-green emitters in various optoelectronic devices.

Acknowledgment. This work was supported by the National Science Foundation, Division of Materials Research. This material is based upon work supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001088.

Supporting Information Available: Complete experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Bunz, U. H. F. *Macromol. Rapid Commun.* **2009**, *30*, 772–805. (b) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.
(2) (a) Burnworth, M.; Rowan, S. J.; Weder, C. *Chem.—Eur. J.* **2007**, *13*, 7828. (b) Knapton, D.; Burnworth, M.; Rowan, S. J.; Weder, C. *Angew. Chem.* **2006**, *45*, 5825. (c) Zhang, S. W.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 3420.
(3) Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulović, V.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 5659–5666.
(4) (a) Taylor, M. S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8480–8483. (b) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048. (c) Baumgarten, M.; Müller, U.; Bohnen, A.; Müllen, K. *Angew. Chem.* **1992**, *104*, 482–485. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 448−451. (d) Weitzel, H.-P.; Bohnen, A.; Müllen, K. *Makromol. Chem.* **1990**, *191*, 2815–2835. (e) Weitzel, H.-P.; Müllen, K. *Makromol. Chem.* **1990**, *191*, 2837–2851. (f) Heun, S.; Bässler, H.; Müller, U.; Müllen, K. *J. Phys. Chem.* **1994**, *98*, 7355–7358. (g) Ishow, E.; Bouffard, J.; Kim, Y.; Swager, T. M. *Macromolecules* **2006**, *39*, 7854–7858. (h) Egbe, D. A. M.; Cornelia, B.; Nowotny, J.; Günther, W.; Klemm, E. *Macromolecules* **2003**, *36*, 5459–5469. (i) Kaneko, T.; Matsubara, T.; Aoki, T. *Chem. Mater.* **2002**, *14*, 3898–3906. (j) Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot, J.-Y. *Macromolecules* **1997**, *30*, 1964–1972. (k) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886–4893. (l) Yang, C.; Jacob, J.; Müllen, K. *Macromolecules* **2006**, *39*, 5696–5704.
(5) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087–12088.
(6) Rose, A.; Lugmair, C. G.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 11298–11299.
(7) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–3772.
(8) (a) Zhu, Z.; Swager, T. M. *Org. Lett.* **2001**, *3*, 3471–3474. (b) Zhao, D.; Swager, T. M. *Macromolecules* **2005**, *38*, 9377–9384.
(9) (a) Olmsted, J., III *J. Phys. Chem.* **1979**, *83*, 2581–2584. (b) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024. (c) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229–235. (d) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251–3260.
(10) Melhuish, W. H. *J. Opt. Soc. Am.* **1964**, *52*, 183–186.
(11) (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322. (b) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873. (c) Bouffard, J.; Swager, T. M. *Macromolecules* **2008**, *41*, 5559–5562.