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Two-Dimensional Scaffolds for the Parallel Alignment of Rod-Shaped Conjugated Molecules

Zhenzhen Dong, Xiaozhong Liu, Glenn P. A. Yap,† and Joseph M. Fox*

Brown Laboratories, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

jmfox@udel.edu

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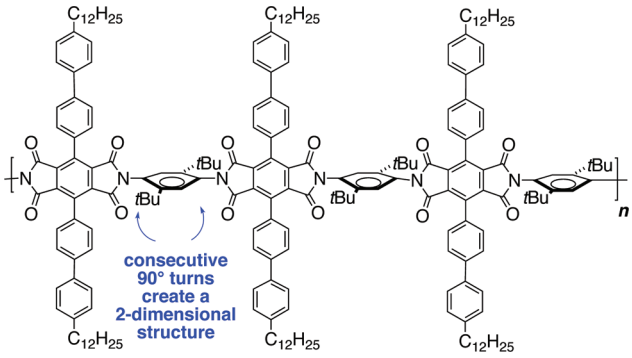

Described is a method for creating two-dimensional, ordered arrays of linear, conjugated organic molecules on polyimide scaffolds. Key to the design was the enforcement of consecutive 90° twist angles along the polyimide backbone. Rod molecules that are templated by such scaffolds are held parallel and in the same plane and have optical properties that are similar to those of monomeric analogues. As supporting evidence for the structures of the polymers, a series of model compounds were synthesized and characterized by X-ray crystallography. The polymeric materials are soluble and have been characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF, and UV−vis spectroscopy.

Introduction

In this contribution, a method for creating two-dimensional, ordered arrays of linear, conjugated organic molecules is described. The concept is depicted in Figure 1 and hinges upon the ability to create scaffolds that can hold conjugated rod molecules in parallel and in the same plane. This strategy is complementary to traditional approaches of creating aligned networks of conjugated molecules (e.g., self-assembly), as rod molecules on scaffolds are held apart by ∼1.1 nm and have electronic properties similar to those of monomeric analogues. Potential applications for such scaffolds include the organization of sensory polymers and nonlinear optical (NLO) chromophores and in the creation of parallel circuits based on molecular wires.

Supramolecular organization has a direct impact on the properties of conjugated organic molecules and on their subsequent utility in applied technologies (e.g., sensory devices,[1−3] polarized electroluminescence devices,[4] field-effect transistors,[5,6] organic light-emitting diodes,[7] and nonlinear optical materials).[8,9]

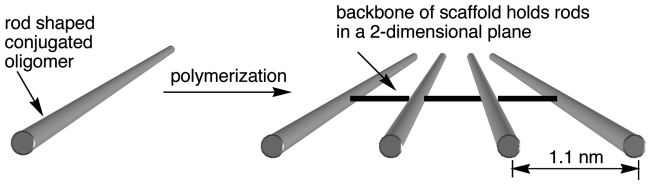

FIGURE 1. Strategy for the creation of ordered, 2-D arrays of conjugated molecules.

† Questions regarding X-ray should be addressed to Dr. Yap (gpyap@chem.udel.edu).

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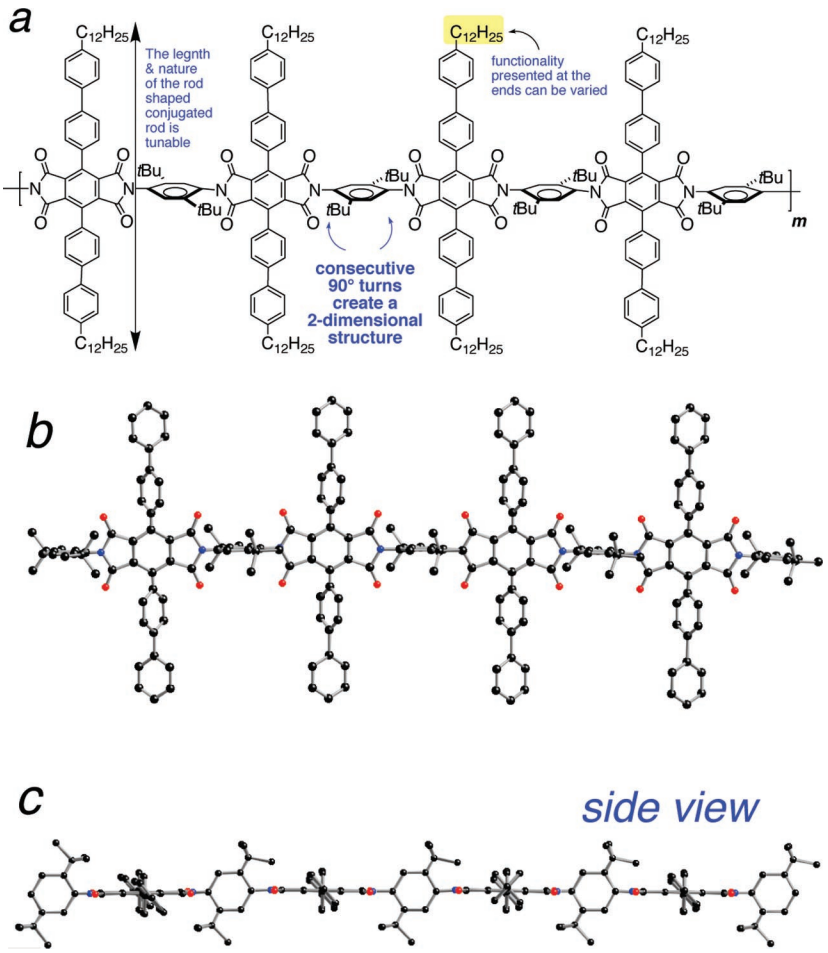

FIGURE 2. (a) Design of two-dimensional templates for parallel alignment of conjugated rod molecules. Two views of a molecular diagram for a segment of this polymer illustrates (b) the parallel alignment of the rods and (c) the planarity of the structure.

There are a number of highly successful strategies for creating organized assemblies of conjugated molecules. The controlled assembly of molecules onto surfaces (e.g., into monolayers[10,11]) is a widely employed approach for controlling the relative molecular orientation of molecules, including conjugated molecules,[12] and modern lithiographic techniques can be used to create oriented patterns with line widths on the nanoscale.[13−16] Noncovalent molecular self-assembly can also result in unusual and enhanced properties relative to those of nonaggregated molecules.[17] Furthermore, liquid crystalline media can be used to orient conducting polymers and oligomers.[18] A feature that is common to these approaches is that the organization is imposed through direct contact with a neighboring molecule and/or by epitaxial alignment by a surface.

While a closely packed arrangement is desirable for many applications, there are notable exceptions. For example, second order NLO chromophores typically require alignment within a polymer matrix (poling) in order to be efficient, but the aggregation of those chromophores dramatically decreases the efficiency of the poling process.[8] A closely packed arrangement can also have a deleterious impact on the highly conjugated polymers that are used in fluorescence-based sensors. Although intermolecular energy migration can be most efficient in molecularly ordered films or aggregates, the close interaction of such polymers will quench fluorescence.[1] Swager has developed an elegant method that minimizes fluorescence quenching by incorporating hindered iptycenes into the backbones of the conjugated polymers.[19,20] While exciton migration through conjugated polymers is obviously an extremely complex phenomenon, it is clear that controlling alignment and patterning has a profound effect. Finally, it is pointed out that the scaffolds proposed in Figure 1 could be used to create insulated, parallel circuits from molecular components and thereby have applica-

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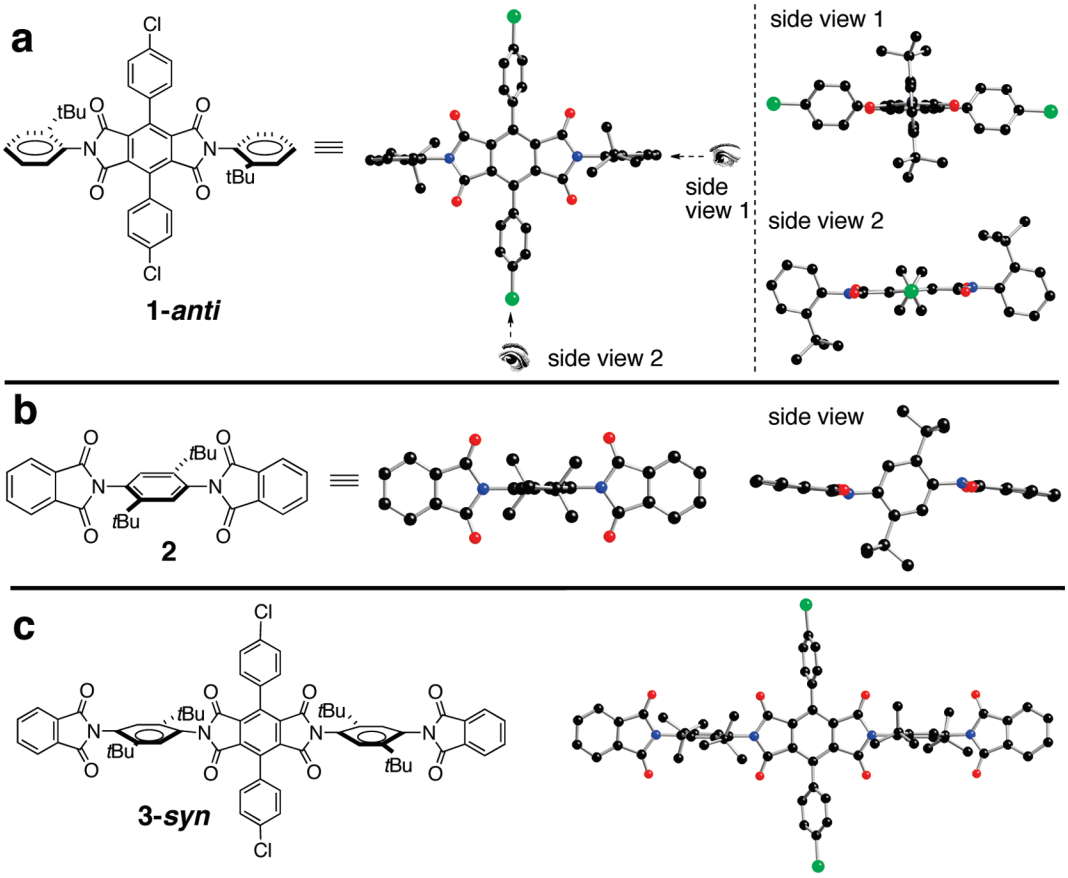

FIGURE 3. Molecular diagrams of crystallographically characterized model compounds for which alternating aromatic subunits are held in the same plane. Steric interactions between the *tert*-butyl group and the imide carbonyls constrain the twist angle between neighboring aromatics to 90°.

tion in the fabrication of devices based on molecular electronics.[21]

We envisioned that the concept in Figure 1 could be realized by synthesizing two-dimensional materials that can align linear, conjugated molecules along the backbone of a linear polyimide. As shown in Figure 2, the key to the design is that consecutive 90° twist angles along the polyimide backbone ensure that adjacent oligomers are held in the same plane. Herein, we describe the successful execution of this strategy. The design is flexible and can be used as a scaffold for linear, conjugated molecules [e.g., oligophenylenes and oligo(phenylene ethynylene)s]. The polymers synthesized in this work are soluble and have been characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry (MALDI-TOF), and UV−vis spectroscopy.

Results and Discussion

As supporting evidence for the structures of the polymers, a series of model compounds have been synthesized and characterized both in solution and by X-ray crystallography. The structures of three compounds (**1**−**3**) are shown in Figure 3. Synthesis of **1**−**3** involves condensation of the appropriate anilines and phthalic or pyromellitic acid derivatives (described in the Supporting Information). In each structure, the *tert*-butylbenzene groups are nearly perpendicular to the phthalimide or pyromellitimide groups. Their structures (after the hydrogens were added using Chem3D) show that there are already van der Waals contacts between the *tert*-butyl hydrogens and the carbonyl oxygens. Thus, any significant deviation from a 90° twist angle[22] would invoke a severe steric penalty. Curran has elegantly shown that chiral *ortho*-(*tert*-butyl)phenylmaleimides are resolvable at room temperature.[23−25] The crystal structure of *N*-(2,5-di-*tert*-butylphenyl)maleimide was determined, and it was shown that the maleimide and aromatic rings were perpendicular.[25] A study by Kishikawa and co-workers also supports the design in Figure 2.[26] These workers synthesized *N*,*N*-bis(2-*tert*-butylphenyl)pyromellitic bisimide for the preparation of inclusion complexes. A variety of host/guest complexes were crystallized, and in each case, the phenyl groups were held fixed in the same plane.

For the preparations of **1** and **3**, the condensations produce approximately equal amounts of two diastereomers (designated as *anti* or *syn*, in reference to the facial alignment of the *tert*-butyl groups that are closest to the pyromellitimide). In the case of **1**, only the *anti*-diastereomer crystallized, whereas the *syn*-diastereomer crystallized for **3**. Comparison of their crystal

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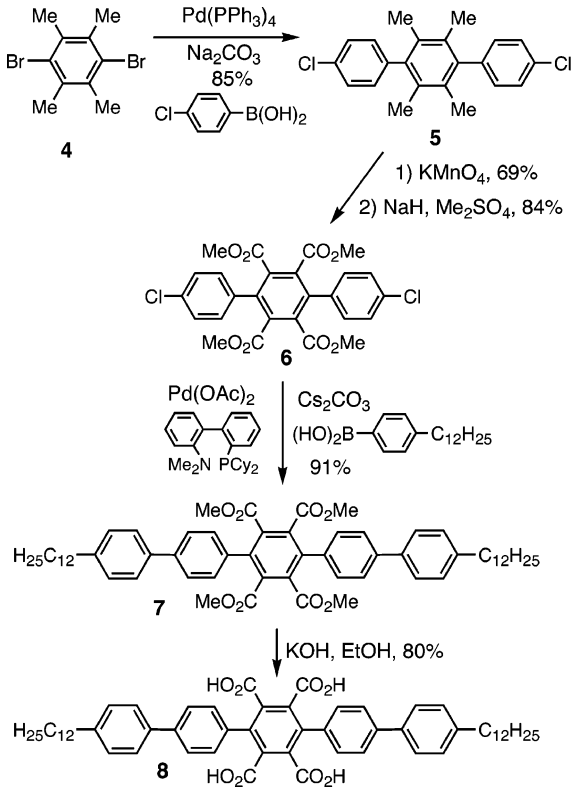
structures shows that the twist angle is not effected significantly by the relative orientation (*syn* vs *anti*) of the *tert*-butyl groups for **1** and **3**, respectively. As shown in the crystal structure of **3**, the distance between the *tert*-butyl groups is large enough so that their *syn*-orientation has very little influence on the twist angle, although it does impose minor out-of-plane bending between the phthalimides and the central core. Importantly, it can be inferred that the stereochemical relationship of the *tert*-butyl groups will not affect the coplanar orientation of alternating subunits within polymers.

Preparation of Co-monomers. Co-monomer **8** was prepared as shown in Scheme 1. The synthesis takes advantage of the low reactivity of arylchlorides toward oxidative addition with many Pd catalysts [e.g., $(PPh_3)_nPd$].[27] Thus, it was possible to selectively couple dibromide **4** with 4-chlorophenylboronic acid to produce dichloride **5**. The 4-chlorophenyl groups of **5** survive the harsh conditions of $KMnO_4$ oxidation and subsequent alkylation to give **6**. Recently developed methods for Pd-catalyzed cross-coupling enable efficient reactions of arylchlorides when specialized ligands are utilized. We have found 2-dicyclohexylphosphino-2′-*N*,*N*-dimethylaminobiphenyl/Pd-$(OAc)_2$-catalyzed Suzuki reactions of **6** to be particularly efficient.[28,29] Thus, the quinquephenyl-derived co-monomer **8** could be prepared via reaction of **6** with 4-dodecylphenylboronic acid and subsequent saponification. Polymeric materials derived from monomer **8** are described in this work. However, it is also demonstrated that the cross-coupling strategy used to prepare **6** can also be employed to prepare co-monomers with extended conjugation (Scheme 2). Thus, the extended co-monomer **10** could be prepared from **6** via a sequence of Suzuki coupling with 4-(triisopropylsilylethynyl)phenylboronic acid, alkyne deprotection, and Sonogashira−Heck−Cassar coupling with 4-dodecylphenylboronic acid. Much longer co-monomers should be available through this synthetic strategy, as rod-shaped oligophenylene ethynylenes are readily prepared by the convergent/divergent methods pioneered by Tour[30−34] and Moore.[35−37]

Model Studies for Polymerization. Polyimides are a commercially important class of materials that have exceptional thermal stability, high mechanical strength, excellent electrical properties, and chemical resistance.[38−40] Accordingly, a number of methods have been developed for their synthesis.[38] While polyimides from 3,6-diphenylpyromellitic anhydride were known,[41−48] it was unclear if conventional methods would be effective for the synthesis of polyimides from sterically demanding 2,5-di-*tert*-butyl-1,4-phenylenediamine. In particular, we considered that isoimide formation might compete with imide formation.[38,49] As a model for the polymerization reaction, we screened a variety of conditions for the coupling of phthalic acid with 2,5-di-*tert*-butyl-1,4-phenylenediamine. For the reaction to be useful in polymerization, it is essential to produce only the imide linkage in high yield (Scheme 3). After screening a variety of conditions, the best results were obtained by simply heating phthalic acid and the diamine in acetic acid at 100 °C. Phthalimide **11** was produced in excellent yield, and the isoimide **12** was not detected. Analogously, heating phthalic anhydride (2 equiv) with 2,5-di-*tert*-butyl-1,4-phenylenediamine cleanly gave bisphthalimide **2**, as shown in Scheme 4, without isoimide side products. A host of other conditions were also screened for the reactions shown in Schemes 3 and 4.[50] However, simple

SCHEME 1. Synthesis of Co-monomer 8



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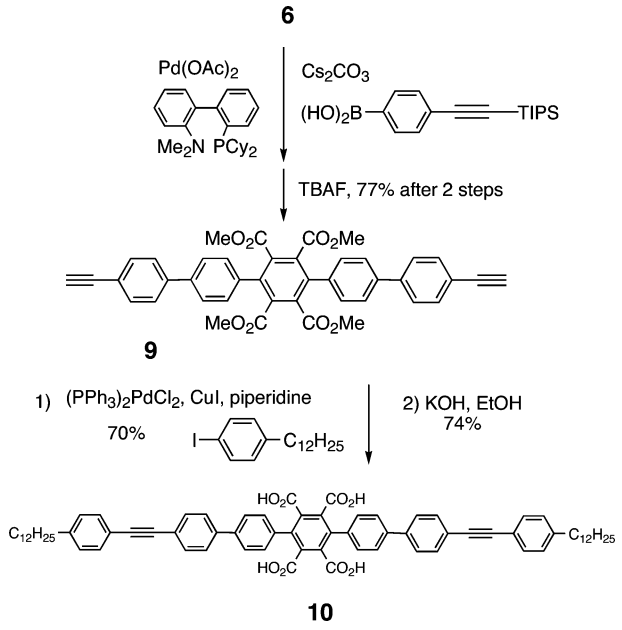
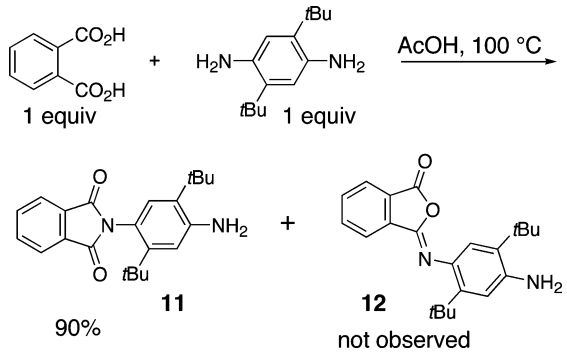
(50) The following conditions were also explored: reflux in THF; reflux in diglyme; reflux in xylene; heating (150 °C) in *m*-cresol (with and without molecular sieves); heating (150 °C) in anisole; heating (100 °C) with NaOAc and Ac_2O; reflux in CH_2Cl_2 with DCC and DMAP.

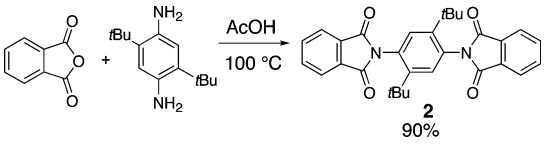
SCHEME 2. Synthesis of Pyromellitic Acid Derivatives with Extended Conjugation



SCHEME 3. Optimized Conditions for the Condensation of Phthalic Acid with 2,5-Di-*tert*-butyl-1,4-phenylenediamine



SCHEME 4. Optimized Conditions for the Condensation of Phthalic Anhydride (2 equiv) with 2,5-Di-*tert*-butyl-1,4-phenylenediamine



heating in acetic acid was superior in terms of both yield and selectivity for imide formation. For example, the EDC/DMAP-mediated reaction of phthalic acid (1 equiv) with 2,5-di-*tert*-butyl-1,4-phenylenediamine (1 equiv, reflux in CH_2Cl_2) produced **11** in only 73% yield, along with 16% of isoimide **12**.

Polymerization Studies. The optimal conditions for the synthesis of model compounds **2** and **11** were next applied to the synthesis of polymeric materials. Heating tetraacid **8** with 2,5-di-*tert*-butyl-1,4-phenylenediamine for 4 days at 100 °C in acetic acid (Scheme 5) gave a polymeric material assigned to structure **13** (Scheme 5). The polymer is freely soluble in many common organic solvents, including $CHCl_3$, CH_2Cl_2, and THF. Evidence for the structure assigned to polymer **13** is the following: (1) The ^{1}H NMR spectrum of **13** (displayed in the Supporting Information) shows resonances for the side-chain

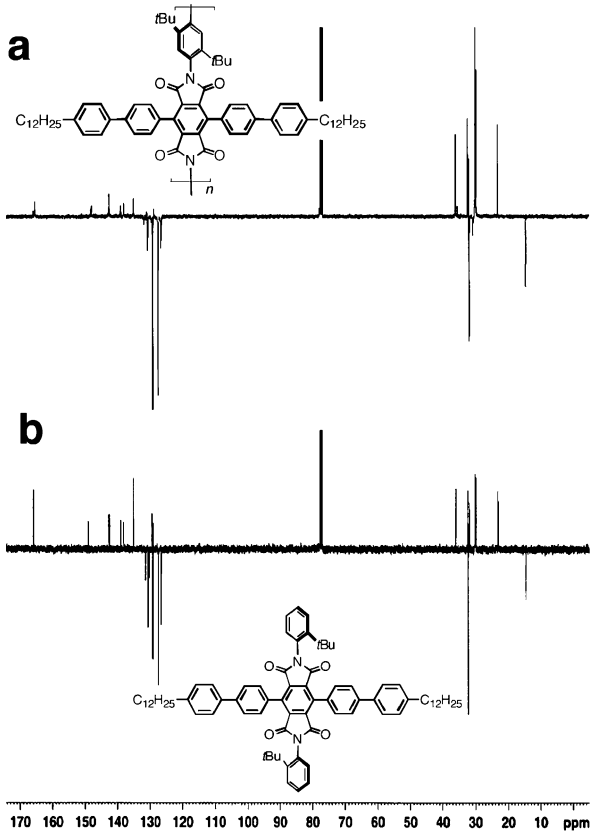
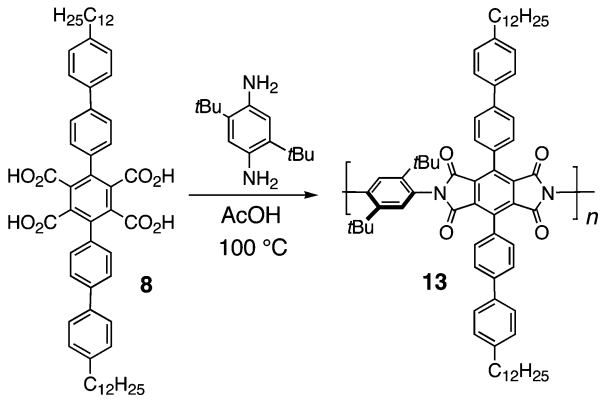


FIGURE 4. ^{13}C NMR spectra of (a) polymer **13** and (b) model compound **14**. Multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear "up"; methine and methyl carbons appear "down".

SCHEME 5. Preparation of Polymer 13



protons and aromatic protons in intensity ratios that are appropriate. Also, the chemical shifts correlate to those of model compound **14**, with the exception that the spectrum of the polymer is broad. (2) The phase-sensitive ^{13}C NMR (APT) spectrum of polymer **13** (Figure 4) shows peaks attributable to the carbonyls of the imides (ca. 166 ppm), the aromatic carbons (ca. 127−150 ppm), the *tert*-butyl groups (ca. 32 and 36 ppm), and the side chains (ca. 14, 23, 30, and 32 ppm). The position and phase of those peaks were analogous to those observed for model compound **14**. (3) The MALDI-TOF mass spectrum shows peaks that correspond to two types of polymeric structures (Figure 5). The peaks labeled a−g are assigned to polymeric structures with up to 7 repeat units that are capped at the ends by acetanilide functions. The peaks labeled h−l are assigned

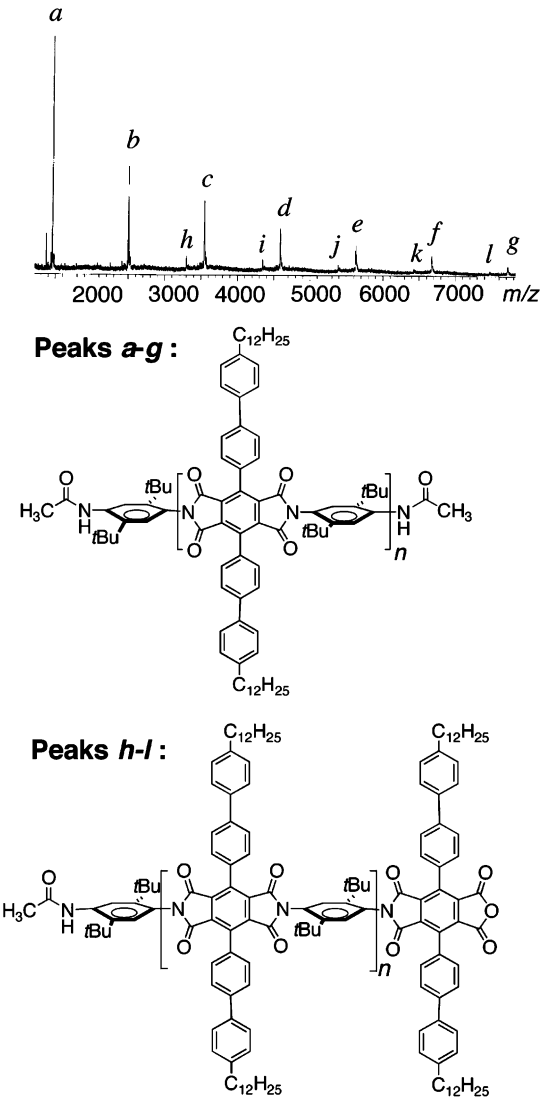


FIGURE 5. MALDI-TOF mass spectrum of polymer **13**. Two types of end groups were identified. Although MALDI-TOF provides absolute molecular weights of oligomers within the mixture, it does not provide a measure of M_w distribution. ^{1}H NMR end group analysis suggests that the polymer contains an average of ~7 repeat units (M_n ~ 7400).

to structures with up to 6 repeat units that are capped by a phthalic anhydride on one end and an acetanilide function on the other end. Table 1 shows that the observed data correlate (±1 Da) with the expected mass spectrum. Although the MALDI-TOF mass spectrum provides evidence of structure, it does not provide a measure of the molecular weight distribution. For polydisperse samples (PDI > 1.2), MALDI is known to underestimate the higher mass polymer distribution, and there is often an upper mass limit above which individual oligomers cannot be distinguished.[51,52] The number-average molecular weight (M_n) of polymer **13** could be estimated by end group analysis of the ^{1}H NMR spectrum. Thus, the number of repeat units in the polymer was estimated to be 7 (M_n ~ 7400) by comparing the integrals of peaks assignable to the acetate end groups (2.3 ppm) and the benzylic methylenes (2.7 ppm) of the repeat unit. For the end group analysis, it was estimated

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TABLE 1. Calculated and Observed Peaks in the MALDI-TOF Spectrum of Polymer 13

structure	formula	*m/z* (calcd)	*m/z* (obsd)
13a ($n = 1$)	$C_{90}H_{114}N_4O_6Ag$	1453.8[a]	1454.2[a]
13b ($n = 2$)	$C_{162}H_{200}N_6O_{10}Ag$	2499.2	2499.7
13c ($n = 3$)	$C_{234}H_{286}N_8O_{14}Ag$	3542.7	3543.4
13d ($n = 4$)	$C_{306}H_{372}N_{10}O_{18}Ag$	4586.2	4586.8
13e ($n = 5$)	$C_{378}H_{458}N_{12}O_{22}Ag$	5629.6	5630.3
13f ($n = 6$)	$C_{450}H_{544}N_{14}O_{26}Ag$	6673.1	6673.5
13g ($n = 7$)	$C_{522}H_{630}N_{16}O_{30}Ag$	7716.5	7716.7
13h ($n = 2$)	$C_{218}H_{262}N_6O_{14}Ag$	3298.3	3298.8
13i ($n = 3$)	$C_{290}H_{348}N_8O_{18}Ag$	4341.8	4342.5
13j ($n = 4$)	$C_{362}H_{434}N_{10}O_{22}Ag$	5385.2	5386.2
13k ($n = 5$)	$C_{434}H_{520}N_{12}O_{26}Ag$	6428.7	6429.2
13l ($n = 6$)	$C_{506}H_{606}N_{14}O_{30}Ag$	7472.2	7472.3

[a] The calculated mass of **13a** is based on monoisotopic mass. The calculated masses of **13b**−**13l** were based on average mass.

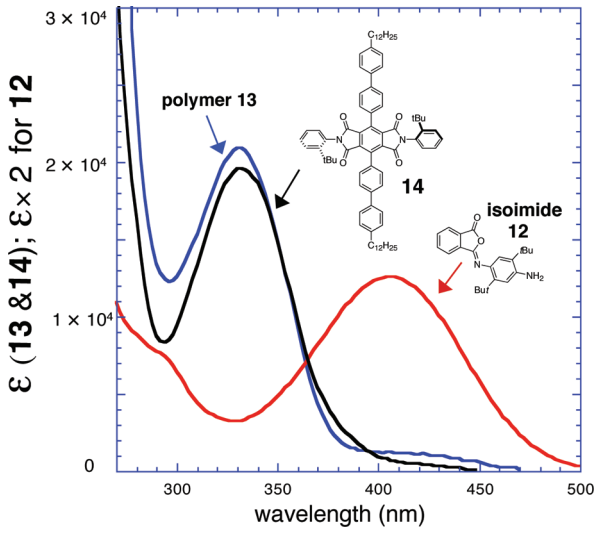

FIGURE 6. Comparison of the UV−vis absorption spectra of polymer **13** (blue line, 1.0 × 10^{-5} M) to model compound **14** (black line, 1.0 × 10^{-5} M) and isoimide **12** (red line, 1.0 × 10^{-4} M).

(from the MALDI-TOF data) that ~80% of the polymers were capped at both ends with acetanilide functions, and that the other 20% had one acetanilide and one phthalic anhydride.

The UV−vis absorption spectra for polymer **13**, model compound **14**, and isoimide **12** were recorded and are displayed in Figure 6. The spectra of the polymer and **14** are very similar and provide evidence that there is negligible conjugation between adjacent quinquephenyls along the backbone of polymer **13**. Comparison was made to the UV−vis spectrum of **12** to verify that the polymerization created imide linkages and not isoimide linkages. In Figure 6, the spectrum of the isoimide is displayed on twice the scale because the model (**14**) and the polymer (**13**) have two imide functions, whereas **12** has only one isoimide. As displayed in Figure 6, the isoimide **12** has an absorption maximum at 405 nm (ϵ = 6333). In contrast, the polymer **13** and model **14** absorb only weakly at this wavelength (ϵ = 1250 and 750, respectively). It can be conservatively estimated that >95% of the linkages in the polymer are imides, and that isoimides account for not more than 5% of the linkages.

The crystal structures of **1** and **3** also show that the aromatic groups directly attached to the pyromellitimide are twisted out of plane relative to the core. For example, twist angles for each of the biphenyl moieties of **1** are 55° in the crystal. Conjugation through biphenyl linkages is attenuated, but not eliminated, by

twist angles of this magnitude.[22] Future studies will involve the preparation of scaffolds in which the quinquephenyls of polymer **13** are replaced by oligo(phenylene ethynylenes), so that conjugation will not be affected by the steric influence of the amide carbonyls.

Conclusion

In conclusion, a strategy for the coplanar alignment of conjugated, rod-shaped organic oligomers on a polyimide template has been described. The structures are supported by their ^{1}H NMR, ^{13}C NMR, MALDI-TOF, UV−vis spectra and by analogy to a number of smaller molecules that have been characterized by X-ray crystallography. Although oligomers are held rigidly in the same plane, their electronic spectra suggest that conjugation is minimal. Future work will involve the incorporation of longer rod molecules onto polyimide templates and in the application of templated rod molecules in molecular electronics and nonlinear optics.

Experimental Section

***N,N′*-Di(2-*tert*-butylphenyl)-3,6-di(4-chlorophenyl)pyromellitimide (1).** A resealable test tube was charged with 2-*tert*-butylaniline (27 mg, 0.18 mmol), 3,6-di(4-chlorophenyl)pyromellitic acid (43 mg, 0.09 mmol), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (0.07 g, 0.36 mmol), 4-dimethylaminopyridine (0.02 g, 0.18 mmol), and dry CH_2Cl_2 (2 mL). The test tube was capped, and the reaction mixture was allowed to stir with heating at 60 °C for 16 h. The mixture was washed with water, dried over $MgSO_4$, concentrated, and chromatographed to give the *syn* and *anti* products as light yellow solids. The yield of the mixture of diastereomers was 60 mg (94%), mp >290 °C. Pure ***anti*-1** could be obtained by crystallization from hexane/CH_2Cl_2. The purity was measured to be ≥95% by ^{1}H NMR. Spectral data for ***anti*-1**: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.61 (dd, J = 8.0, 1.4 Hz, 2H), 7.48−7.50 (m, 8H), 7.42 (app dt, J = 7.3, 1.5 Hz, 2H), 7.29 (app dt, J = 7.3, 1.5 Hz, 2H), 6.97 (dd, J = 8.0, 1.4 Hz, 2H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 165.8 (u), 149.3 (u), 138.1 (u), 136.3 (u), 135.2 (u), 131.5 (dn), 131.4 (dn), 130.5 (dn), 129.4 (u), 129.1 (dn), 128.8 (u), 128.5 (dn), 127.7 (dn), 36.0 (u), 32.2 (dn); IR (cm^{-1}) 2964, 1766, 1722, 1713, 1369, 1130, 1077, 896, 838, 770, 761, 732, 630; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{42}H_{34}N_2O_4Cl_2$, 723.1793; found, 723.1778; UV−vis (2×10^{-5} M in CH_2Cl_2) λ_{max} 244, 332.

2,5-Di-*tert*-butyl-1,4-diphthalimido Benzene (2). A resealable test tube was flushed with N_2 and charged with phthalic acid (15 mg, 0.090 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine[53] (10 mg, 0.045 mmol), and glacial acetic acid (0.5 mL). The test tube was capped, and the reaction mixture was allowed to stir with heating at 100 °C for 24 h. Water (10 mL) was added to the mixture. A precipitate was filtered on a Buchner funnel and dried under vacuum to give the title product as a white solid. The yield was 20 mg (90%), mp >290 °C. The purity was measured to be 93% by ^{1}H NMR. Crystals of **2** were grown from CH_2Cl_2/hexane: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.97−8.00 (m, 4H), 7.81−7.83 (m, 4H), 7.16 (s, 2H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 168.9 (u), 148.7 (u), 134.9 (dn), 132.7 (u), 132.3 (dn), 131.4 (u), 124.3 (dn), 35.6 (u), 31.8 (dn); IR (cm^{-1}) 2980, 1709, 1696, 1506, 1385, 1320, 1268, 1104, 1082, 868, 714, 694; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{30}H_{28}N_2O_4$, 503.1947; found, 503.1938; UV−vis (1×10^{-4} M in CH_2Cl_2) λ_{max} 235, 293.

***N,N′*-Di(4-phthalimido-2,5-di-*tert*-butylphenyl)-3,6-di(4-chlorophenyl)pyromellitimide (3).** A resealable test tube was charged with 3,6-di(4-chlorophenyl)pyromellitic acid (7.6 mg, 0.016 mmol), compound **11** (11.2 mg, 0.032 mmol), and glacial acetic acid (1.0 mL). The test tube was flushed with N_2 and capped, and the reaction mixture was allowed to stir with heating at 100 °C for 24 h. Water (10 mL) was added to the mixture, and a precipitate was filtered and chromatographed (50% ethyl acetate/hexane) to give a ∼1:1 mixture of ***syn*-** and ***anti*-3** as a light yellow solid. The yield was 16 mg (92%), mp >290 °C. The purity was measured to be ≥95% by ^{1}H NMR. Pure ***syn*-3** could be obtained by crystallization from DMF/hexane. Spectral properties of the *syn*/*anti* mixture: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.94−7.96 (m, 4H), 7.80−7.82 (m, 4H), 7.49−7.51 (m, 8H), 7.07−7.11 (m, 4H), 1.20−1.28 (m, 36H); The ^{13}C NMR spectrum of the mixture of diastereomers is displayed; IR (cm^{-1}) 2964, 2916, 2850, 1773, 1724, 1390, 1265, 1130, 1103, 1081, 1015, 839, 821, 721, 668; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{66}H_{56}O_8N_4Cl_2$, 1125.3373; found, 1125.3347; UV−vis (1×10^{-5} M in CH_2Cl_2) λ_{max} 229, 274.

1,4-Di(4-chlorophenyl)-2,3,5,6-tetramethyl Benzene (5). 1,4-Dibromo-2,3,5,6-tetramethylbenzene[54] (**4**) (3.71 g, 12.7 mmol), *p*-chlorophenylboronic acid (7.93 g, 50.8 mmol), $Pd(PPh_3)_4$ (0.144 g, 1.23 mmol), and Na_2CO_3 (6.51 g, 61.4 mmol) were dissolved in toluene (80 mL) and water (80 mL). The mixture was allowed to reflux under N_2 for 3 days. The mixture was then cooled, and the aqueous layer was extracted with toluene. The combined extracts were dried over $MgSO_4$, filtered, and concentrated. Crystallization from cold ethyl acetate gave the title compound as a white solid. The yield was 3.83 g (85%), mp >290 °C. The purity was measured to be 94% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.45−7.48 (m, 4H), 7.15−7.17 (m, 4H), 1.99 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 141.4 (u), 140.7 (u), 132.8 (u), 132.4 (u), 131.3 (dn), 129.0 (dn), 18.5 (dn); IR (cm^{-1}) 1493, 1460, 1090, 1016, 988, 864, 813; HRMS (ESI+) *m/z* [M+], calcd for $C_{22}H_{20}Cl_2$, 354.0942; found, 354.0925.

3,6-Di(4-chlorophenyl)pyromellitic Acid. Compound **5** (3.82 g, 10.8 mmol) and $KMnO_4$ (8.67 g, 54.9 mmol) were heated in pyridine (125 mL) and water (16 mL) at reflux temperature under N_2 for 2 days. The mixture was filtered and concentrated. Additional $KMnO_4$ (8.67 g, 54.9 mmol) and NaOH (7.23 g, 181 mmol) were added to the mixture, which was again allowed to reflux in water (150 mL) for 16 h. EtOH (15 mL) was carefully added to the mixture to destroy excess $KMnO_4$. The mixture was filtered, washed with water, and acidified (10% HCl). The white solid which precipitated was filtered, washed with water, and dried under vacuum. The title product was obtained as a white solid. The yield was 3.54 g (69%), mp >290 °C. The purity was measured to be 92% by ^{1}H NMR: ^{1}H NMR (400 MHz, acetone-d_6, δ) 7.48−7.60 (m, 4H), 7.38−7.41 (m, 4H); ^{13}C NMR (100 MHz, acetone-d_6, δ) 167.5 (u), 136.6 (u), 136,5 (u) 135.2 (u), 134.2 (u), 131.1 (dn), 128.5 (dn); IR (cm^{-1}) 1712, 1695, 1225, 856, 728.

Tetramethyl Di(4-chlorophenyl)pyromellitate (6). A solution of compound 3,6-di(4-chlorophenyl)pyromellitic acid (4.90 g, 10.3 mmol) in *N*,*N*-dimethylacetamide (DMA, 150 mL) was cooled by an ice/water bath. NaH (1.86 g, 46.4 mmol) was added to this solution, and the reaction mixture was allowed to stir at 0 °C for 15 min. Me_2SO_4 (10.0 mL, 103 mmol) was added to the mixture via syringe. The ice bath was removed, and the reaction was allowed to warm to rt while stirring under N_2 for 16 h. The reaction was then quenched by saturated NH_4Cl(aq). The mixture was extracted with CH_2Cl_2 (100 mL × 3) and concentrated. The DMA was removed by distillation at 100 °C under vacuum. The mixture was chromatographed (1:1 CH_2Cl_2:ethyl acetate) and dried under vacuum to give the title product as a white solid. The yield was 4.62 g (84%), mp >290 °C. The purity was measured to be ≥95% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.37−7.39 (m, 4H), 7.18−7.20 (m, 4H), 3.54 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 167.2 (u), 137.9 (u), 135.5 (u), 135.1 (u), 135.0 (u), 130.1 (dn), 129.0 (dn), 53.2 (dn); IR (cm^{-1}) 1728, 1714, 1444, 1329, 1208,

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1170, 1078, 1013, 979, 860, 730; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{26}H_{20}O_8Cl_2$, 553.0433; found, 553.0406.

Tetramethyl 3,6-Bis[4′-dodecyl-(1,1′-biphenyl)-4-yl]pyromellitate (7). A mixture of compound **6** (1.35 g, 2.54 mmol), (4-dodecylphenyl)boronic acid (7.27 g, 25.07 mmol), 2-dicyclohexylphosphino-2′-*N*,*N*-dimethylaminobiphenyl (79 mg, 0.20 mmol), $Pd(OAc)_2$ (23 mg, 0.10 mmol), Cs_2CO_3 (3.27 g, 10.04 mmol), and 1,4-dioxane (70 mL) was heated at 60 °C under N_2 for 5 days. The mixture was then filtered, concentrated, chromatographed (first with 1:10 ethyl acetate:hexane, then with 1:20 ethyl acetate:CH_2Cl_2), and dried under vacuum to give the title product as a white solid. The yield was 2.20 g (91%), mp >290 °C. The purity was measured to be ≥95% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.67−7.70 (m, 4H), 7.60−7.62 (m, 4H), 7.35−7.38 (m, 4H), 7.31−7.33 (m, 4H), 3.57 (s, 12H), 2.70 (t, J = 7.5 Hz, 4H), 1.70 (m, 4H), 1.31−1.38 (m, 36H), 0.93 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 167.7 (u), 143.1 (u), 141.2 (u), 138.5 (u), 137.9 (u), 135.9 (u), 135.0 (u), 129.4 (dn), 129.2 (dn), 127.3 (dn), 127.0 (dn), 53.0 (dn), 36.0 (u), 32.3 (u), 31.9 (u), 30.10 (2C, u), 30.07 (u), 30.03 (u), 29.96 (u), 29.78 (2C, u), 23.1 (u), 14.54 (dn); IR (cm^{-1}) 2916, 2850, 1740, 1722, 1442, 1211, 1181, 980, 806, 609; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{62}H_{78}O_8$, 973.5594; found, 973.5574.

3,6-Bis[4′-dodecyl-(1,1′-biphenyl)-4-yl]pyromellitic acid (8). A resealable Schlenk tube was charged with compound **7** (0.32 g, 0.34 mmol), 40% KOH(aq) (2 mL), and EtOH (5 mL). The tube was sealed, and the mixture was heated at 100 °C for 20 h, during which time the product precipitated. The solid was collected by filtration and stirred in a mixture of ~1:1:1 10% HCl, acetone, and CH_2Cl_2 until completely dissolved. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated to give the title product as a white solid. The yield was 0.24 g (80%), mp >290 °C. The purity was measured to be 93% by ^{1}H NMR: ^{1}H NMR (400 MHz, acetone-d_6, δ) 7.68−7.70 (m, 4H), 7.61−7.64 (m, 4H), 7.45−7.47 (m, 4H), 7.30−7.33 (m, 4H), 2.66 (t, J = 7.7 Hz, 4H), 1.63 (m, 4H), 1.27−1.34 (m, 36H), 0.85 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, acetone-d_6, δ) 167.7 (u), 142.7 (u), 141.0 (u), 138.0 (u), 137.0 (u), 136.7 (u), 135.2 (u), 129.9 (dn), 129.4 (dn), 127.1 (dn), 126.6 (dn), 35.7 (u), 32.2 (u), 31.8 (u), 22.8(u), 13.9(dn). We note that seven of the methylene carbons were not identified because they overlap with the acetone-d_6 peak. The solubility of compound **8** in other solvents was not suitable for ^{13}C NMR analysis. IR (cm^{-1}): 2917, 2849, 1713, 1413, 1290, 1184, 1005, 809, 721.

Tetramethyl 3,6-Bis[4′-ethynyl-(1,1′-biphenyl)-4-yl]pyromellitate (9). A dry round-bottomed flask was charged with **6** (0.56 g, 1.05 mmol), 4-(triisopropylsilylethynyl)phenylboronic acid[55] (2.53 g, 8.38 mmol), 2-dicyclohexylphosphino-2′-*N*,*N*-dimethylaminobiphenyl (0.17 g, 0.04 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol), and Cs_2CO_3 (1.36 g, 4.20 mmol). The flask was evacuated and refilled with N_2. 1,4-Dioxane (22 mL) was added, and the mixture was heated at 60 °C under N_2 for 5 days and was then filtered, concentrated, and chromatographed (first with 1:10 ethyl acetate: hexane, then with 1:20 ethyl acetate:CH_2Cl_2). The resulting white solid was stirred in THF (25 mL) at rt. TBAF (4.2 mL, 1.0 M in THF, 4.2 mmol) was slowly added via syringe. The mixture was allowed to stir at rt for 14 h, and the reaction was quenched by 10% HCl. The white precipitate was filtered, washed with water, and dried under vacuum to give the title product as a white solid. The yield was 0.54 g (77%), mp >290 °C. The purity was measured to be ≥95% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.58−7.66 (m, 12H), 7.34−7.36 (m, 4H), 3.55 (s, 12H), 3.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 167.1, 140.5, 140.0, 138.0, 136.2, 134.6, 132.6, 128.9, 126.9, 126.7, 121.4, 83.4, 78.0, 52.7; IR (cm^{-1}) 1738, 1713, 1441, 1329, 1207, 1178, 978, 847, 826, 811, 609; HRMS (ESI+) *m/z* [M + Na], calcd for $C_{42}H_{30}O_8$, 685.1838; found, 685.1814.

Tetramethyl 3,6-Bis[4′-(4-dodecylphenylethynyl)-(1,1′-biphenyl)-4-yl]pyromellitate. A Schlenk tube was charged with compound **9** (10 mg, 0.015 mmol), 1-dodecyl-4-iodobenzene[56] (56 mg, 0.15 mmol), $PdCl_2(PPh_3)_4$ (0.2 mg, 0.0003 mmol), and CuI (0.1 mg, 0.0006 mmol). The tube was evacuated and refilled with N_2. Freshly distilled piperidine (1.5 mL) was added, and the mixture was allowed to stir under N_2 at rt for 3 days, and the mixture was filtered. The filtrate was concentrated and chromatographed (10:4:1 hexane:CH_2Cl_2:ethyl acetate) to give the title product as a white solid. The yield was 12 mg (70%), mp >290 °C. The purity was measured to be 91% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.60−7.68 (m, 12H), 7.46−7.48 (m, 4H), 7.35−7.37 (m, 4H), 7.17−7.18 (m, 4H), 3.55 (s, 12H), 2.62 (t, J = 7.6 Hz, 4H), 1.62 (m, 4H), 1.26−1.32 (m, 36H), 0.88 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 167.6 (u), 144.0 (u), 140.5 (u), 140.1 (u), 138.5 (u), 136.5 (u), 135.0(u), 132.5 (dn), 132.0 (dn), 129.3 (dn), 129.0 (dn), 127.3 (dn), 127.1 (dn), 123.3 (u), 120.7 (u), 91.1 (u), 89.0 (u), 53.2(dn), 36.4 (u), 32.4 (u), 31.7 (u), 30.11 (u), 30.08 (2C, u), 30.02 (u), 29.9 (u), 29.8 (u), 29.7 (u), 23.1 (u), 14.6 (dn); IR (cm^{-1}) 2921, 2852, 1740, 1724, 1437, 1254, 1179, 985, 844, 722. Anal. Calcd for $C_{78}H_{86}O_8$: C, 81.36; H, 7.53. Found: C, 81.33; H, 7.64.

3,6-Bis[4′-(4-dodecylphenylethynyl)-(1,1′-biphenyl)-4-yl]pyromellitic Acid (10). The procedure was identical to that used to prepare compound **8**. Thus, 40 mg of tetramethyl 3,6-bis[4′-(4-dodecylphenylethynyl)-(1,1′-biphenyl)-4-yl]pyromellitate gave 28 mg (74%) of **10** as a white solid, mp >290 °C. The ^{13}C NMR spectrum was measured by HSQC and HMBC because the solubility was too low to directly obtain a high quality ^{13}C NMR spectrum: ^{1}H NMR (400 MHz, acetone-d_6, δ) 7.81−7.84 (m, 8H), 7.67−7.69 (m, 4H), 7.50−7.55 (m, 8H), 7.29−7.31 (m, 4H), 2.68 (t, J = 7.8 Hz, 4H), 1.66 (m, 4H), 1.30−1.41 (m, 36H), 0.90 (t, J = 6.8 Hz, 6H); ^{13}C NMR (detected by HSQC and HMBC, 100 MHz, acetone-d_6, δ) 128.8, 126.4, 124.5, 121.2, 120.7, 119.9, 117.7, 114.9, 113.1, 112.8, 111.4, 110.9, 109.8, 109.7, 93.3, 92.0, 35.9, 32.2, 31.6, 22.9, 13.9. We note that seven of the methylene carbons were not identified because they overlap with the acetone-d_6 peak. The solubility of compound **10** in other solvents was not suitable for ^{13}C NMR analysis. IR (cm^{-1}): 2967, 1737, 1366, 1216, 814.

***N*-(4-Amino-2,5-di-*tert*-butyl)phthalimide (11).** A resealable test tube was flushed with N_2 and charged with phthalic anhydride (40 mg, 0.27 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine[53] (60 mg, 0.27 mmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (50 mg, 0.27 mmol), 4-dimethylaminopyridine (30 mg, 0.27 mmol), and dry CH_2Cl_2 (2 mL). The tube was capped, and the reaction mixture was heated in a bath at 60 °C for 16 h. The mixture was then partitioned between CH_2Cl_2 and water, concentrated, and chromatographed (gradient of 10−40% ethyl acetate/hexane) to give the title product as a white solid. The yield was 70 mg (73%), mp 235−237 °C. The purity was measured to be ≥95% by ^{1}H NMR.

An alternate method to prepare compound **11** was similar to that used to prepare compound **2**. Thus, phthalic anhydride (40 mg, 0.27 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine[53] (60 mg, 0.27 mmol), and glacial acetic acid (2.0 mL) gave 86 mg (90%) of **11**: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.97−7.99 (m, 2H), 7.82−7.83 (m, 2H), 6.85 (s, 1H), 6.79 (s, 1H), 4.06 (br, 2H), 1.41 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 169.7 (u), 147.7 (u), 145.8 (u), 134.6 (dn), 132.86 (u), 132.80 (u), 130.1 (dn), 124.1 (dn), 120.2 (u), 117.9 (dn), 35.3 (u), 34.2 (u), 31.9 (dn), 29.8 (dn); IR (cm^{-1}) 2964, 1779, 1710, 1404, 1391, 1375, 1105, 1081, 873, 729, 714; HRMS (ESI+) *m/z* [M+], calcd for $C_{22}H_{26}N_2O_2$, 350.1994; found, 350.1996.

***N*-(4-Amino-2,5-di-*tert*-butyl)-isophthalimide (12).** A resealable test tube was flushed with N_2 and charged with phthalic anhydride

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(40 mg, 0.27 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine[53] (60 mg, 0.27 mmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (50 mg, 0.27 mmol), 4-dimethylaminopyridine (30 mg, 0.27 mmol), and dry CH_2Cl_2 (2 mL). The tube was capped under N_2, and the reaction mixture was allowed to stir for 16 h at rt. The mixture was then partitioned between CH_2Cl_2 and water. The organics were dried over $MgSO_4$, concentrated, and chromatographed (10−20% ethyl acetate/hexane) to give the title product as a yellow wax. The yield was 50 mg (52%). The purity was measured to be 93% by ^{1}H NMR: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.01−8.03 (m, 1H), 7.96−7.98 (m, 1H), 7.81 (app dt, J = 7.5, 0.6 Hz 1H), 7.70 (app dt, J = 7.5, 0.6 Hz, 1H), 7.48 (s, 1H), 6.68 (s, 1H), 3.89 (br, 2H), 1.46 (s, 9H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 166.3 (u), 145.1 (u), 143.5 (u), 142.3 (u), 138.4 (u), 135.6 (dn), 133.4 (u), 132.6 (dn), 131.6 (u), 127.9 (u), 125.6 (dn), 124.6 (dn), 123.4 (dn), 116.3 (dn), 35.6 (u), 34.4 (u), 31.0 (dn), 30.1 (dn); IR (cm^{-1}) 2967, 2922, 1797, 1732, 1695, 1471, 1364, 1240, 1095, 900, 773, 732, 700; HRMS (ESI+) *m*/*z* [M + H], calcd for $C_{22}H_{26}N_2O_2$, 351.2073; found, 351.2059; UV−vis (1×10^{-4} M in CH_2Cl_2) λ_{max} 229, 405.

Polymer 13. A resealable test tube was flushed was N_2 and charged with compound **8** (50.0 mg, 0.056 mmol), 2,5-di-*tert*-butylbenzene-1,4-diamine[53] (12.3 mg, 0.056 mmol), and glacial acetic acid (2.0 mL). The tube was capped, and the mixture was allowed to stir for 4 days with heating in an oil bath at 100 °C. Water (20 mL) was added to the solution. A precipitate formed and was isolated by filtration and dried under vacuum. The resulting solid was transferred to a resealable test tube that had been flushed with N_2. Sequentially added to the tube were triethylamine (0.02 mL, 0.12 mmol), acetic anhydride (0.02 mL, 0.12 mmol), and CH_2Cl_2 (1.5 mL). The mixture was heated at 60 °C for 16 h, washed with water, dried over $MgSO_4$, filtered, and concentrated. Precipitation from hexane provided polymer **13** as a yellow solid. The yield was 47 mg (75%), mp >290 °C: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.60−7.72 (m, 12H), 7.26−7.28 (m, 4H), 7.04−7.09 (m, 2H), 2.68 (t, J = 6.89 Hz, 4H), 2.25 (s, 0.8H), 1.68 (m, 4H), 1.23−1.39 (m, 54H), 0.92 (t, J = 6.7 Hz, 6H). The ^{13}C NMR spectrum is displayed; IR (cm^{-1}): 2922, 1728, 1506, 1464, 1389, 1347, 1126, 901, 835, Anal. Calcd for $C_{522}H_{630}N_{16}O_{30}$ (formula of 7-mer): C, 82.40; H, 8.35. Found: C, 81.64; H, 8.25; UV−vis (1×10^{-5} M in CH_2Cl_2) λ_{max} 234, 256, 330.

***N*,*N*′-Di(2-*tert*-butylphenyl)-3,6-di[(4′-dodecyl-1,1′-biphenyl)-4-yl]pyromelletimide (14).** The procedure was similar to that used to prepare compound **3**. Thus, 30 mg of **8** gave 35 mg of **14** (93%) as a light yellow solid that was a ∼1:1 mixture of *syn*- and *anti*-isomers. Chromatography (30% ethyl acetate in hexane) separated the diastereomers, mp >290 °C. The purity was measured to be ≥95% by ^{1}H NMR. UV−vis of the mixture of diastereomers (1×10^{-5} M in CH_2Cl_2) λ_{max}: 244, 330. Spectral data for the diastereomer of **14** that eluted more quickly by SiO_2 chromatography: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.72−7.74 (m, 4H), 7.59−7.64 (m, 10H), 7.38−7.42 (m, 2H), 7.24−7.30 (m, 6H), 6.96−6.98 (m, 2H), 2.68 (t, J = 7.6 Hz, 4H), 1.67−1.70 (m, 4H), 1.40 (s, 18H), 1.31−1.37 (m, 36H), 0.92 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 166.1(u), 149.2 (u), 142.8 (u), 142.6 (u), 139.1 (u), 138.3 (u), 135.3 (u), 131.6 (dn), 130.7 (dn), 130.3 (dn), 129.5 (u), 129.22 (dn), 129.18 (u), 129.11 (dn), 127.6 (dn), 127.5 (dn), 126.6 (dn), 36.1 (u), 32.4 (u), 32.2 (dn), 31.9 (u), 30.13 (2C, u), 30.10 (u), 30.05 (u), 29.98 (u), 29.83 (u), 29.82 (2C, u), 23.2 (u), 14.6 (dn). Spectral data for the diastereomer of **14** that eluted more slowly by SiO_2 chromatography: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.67−7.69 (m, 4H), 7.54−7.60 (m, 10H), 7.35−7.39 (m, 2H). 7.23−7.26 (m, 6H), 6.97−6.99 (m, 2H), 2.63 (t, J = 7.6 Hz, 4H), 1.60−1.68 (m, 4H), 1.33 (s, 18H), 1.23−1.33 (m, 36H), 0.89 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 165.6 (u), 148.9 (u), 142.4 (u), 142.2 (u), 138.7 (u), 137.9 (u), 134.8 (u), 131.2 (dn), 130.3 (dn), 129.9 (dn), 129.2 (u), 128.8 (dn), 128.68 (dn), 128.66 (u), 127.2 (dn), 127.1 (dn), 126.2 (dn), 35.7 (u), 31.9 (u), 31.8 (dn), 31.5 (u), 29.7 (2C, u), 29.7 (2C, u), 29.6 (u), 29.56 (u), 29.4 (2C, u) 22.7 (u), 14.2 (dn); IR (cm^{-1}) 2924, 2854, 1768, 1722, 1445, 1371, 1137, 895, 812, 769, 732; HRMS (ESI+) *m*/*z* [M + Na], calcd for $C_{78}H_{92}N_2O_4$, 1143.6955; found, 1143.6927.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra are displayed for all new compounds. The UV−vis spectra (220−600 nm) are provided for compounds **12**−**14**. CIF files for crystallographically characterized compounds are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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