Synthesis of Diacetylene Macrocycles Derived from 1,2-Diethynylbenzene Derivatives: Structure and Reactivity of the Strained Cyclic Dimer

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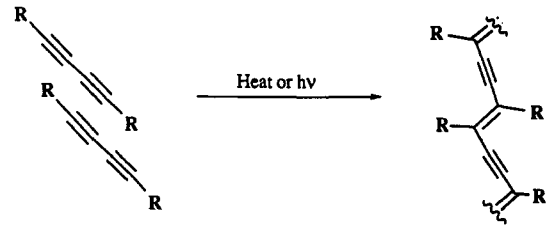
Diacetylene macrocycles **2–4** (n = 1–3) (R = H, C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $OC_{10}H_{21}$) have been prepared from the oxidative coupling of 1,2-diethynylbenzene derivatives. These compounds can be produced in useful quantities and are of interest as precursors to novel conjugated organic polymers. The reported results indicate that when the R groups are large the dimeric macrocycle (n = 1) can be prepared in as high as 74% yield from the corresponding 1,2-diethynylbenzene in a one-step procedure. An alternate multistep procedure was found to produce the tetrameric macrocycle (n = 3, R = C_6H_{13}) in 45% yield. The highly strained dimeric macrocycle was characterized by an X-ray structure and was found to be very reactive. The dimers undergo a rapid very exothermic polymerization at 100–125 °C, indicative of a chain reaction. Reaction of the dimeric macrocycles with iodine results in intramolecular cyclization and a new 20π electron tetraiodide fused ring system. Reaction of the tetraiodide with oxygen produces a related compound in which two of the iodides have been converted to ketones.

Introduction

Organic polymeric materials with extended conjugation, often referred to as conducting polymers, are typically semiconductors in pure form but can exhibit metallic levels of conductivity with oxidative or reductive doping.[1] These types of materials have been the subject of extensive investigations as a result of their potential technological applications. Of all of the organic conducting polymers reported to date, those containing only carbon atoms in the π conjugated system are the most conductive.[2] The interest in carbon-based conductors has been heightened by reports that polyacetylene can exhibit conductivities comparable to copper,[2a] and also by the discovery of superconductivity in n-doped samples of C_{60}.[3]

The high degree of unsaturation associated with compounds containing multiple acetylene groups makes them attractive intermediates for the synthesis of new conjugated polymers, graphite ribbons, and novel allotropes of carbon.[4] Diacetylenes are particularly important in this regard, and the topochemical polymerization of diacetylenes is unique in creating single crystals of organic polymers with conjugated backbones.[5] These types of polymerizations generally occur as shown in eq 1 and are thought to propagate via a biradical species.[6] Diacetylene polymerizations are also of interest as thermochromic indicators,[7] and the resultant polydiacetylenes are known to exhibit nonlinear optical properties and photogenerated carriers with mobilities much higher than other organic polymers.[5a]



(1)

Although polymerizations of acyclic diacetylenes have been studied extensively, few systems incorporating cyclic diacetylenes have been investigated.[8] In an effort to expand the scope of topochemical diacetylene polymerizations, we have been developing cyclic diacetylenes which can be polymerized in crystalline and liquid crystalline phases to yield new kinds of conjugated polymers. We report herein the synthesis of a family of macrocyclic diacetylenes (**2**, **3**, and **4**). Additionally, we discuss the structure and intramolecular cyclization reactions of **2**, a highly strained diacetylene which is under investigation in the development of novel topochemical polymerizations.[9]

Results and Discussion

1,2-Diethynylbenzene derivatives, **1**, were prepared with nickel and palladium cross-coupling procedures as shown

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(8) (a) Baughman, R. H.; Yee, K. C. *J. Polym. Sci.: Polym. Chem.* **1974**, *12*, 2467. (b) Enkelmann, V.; Graf, H. J. *Acta. Crystallogr.* **1978**, *B34*, 3715.

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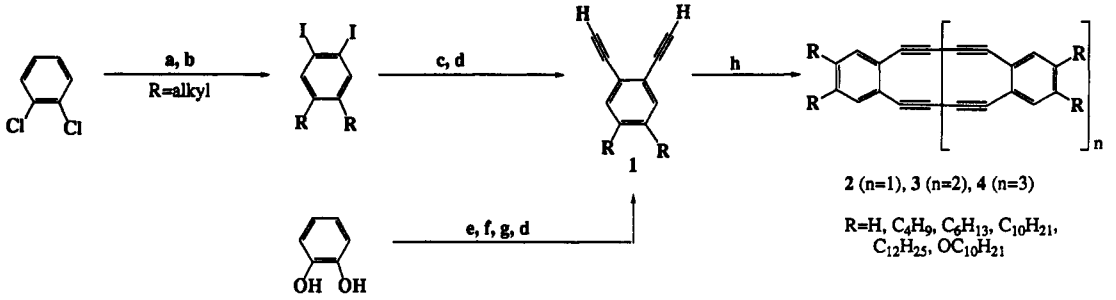
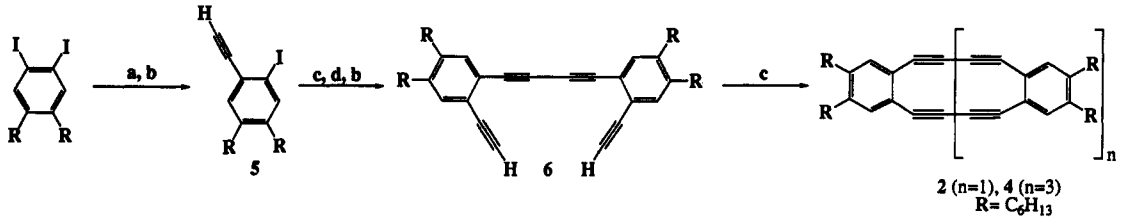
Scheme 1[a]



[a] (a) $H(CH_2)_nMgBr$, $(dppp)NiCl_2$ (cat.); (b) $NaIO_3$, H_2SO_4, HOAc, I_2; (c) TMSA, $(PPh_3)_2PdCl_2$ (5%) CuI (5%), $NH(iPr)_2$, rt; (d) KOH/H_2O, MeOH/THF; (e) $C_{10}H_{21}Br$, K_2CO_3, acetone; (f) $Hg(OAc)_2$, I_2, CH_2Cl_2; (g) TMSA, $(PPh_3)_2PdCl_2$ (5%), CuI (2 equiv), $NH(iPr)_2$, 70 °C; (h) 1.1 equiv of CuCl, 23 equiv of TMEDA, O_2.

Scheme 2[a]



[a] (a) 1 equiv of TMSA, $(PPh_3)_2PdCl_2$ (5%), CuI (5%), $HN(iPr)_2$, rt; (b) KOH/H_2O, MeOH/THF; (c) 1.1 equiv of CuCl, 23 equiv of TMEDA, O_2; (d) 1.2 equiv of TMSA, $(PPh_3)_2PdCl_2$ (5%), CuI (5%), $HN(iPr)_2$ 70 °C.

in Scheme 1. For the R = alkyl derivatives, the palladium-catalyzed cross-coupling reactions between the aryl iodides and (trimethylsily)acetylene proceed in >90% yields with the standard conditions of catalytic (5%) CuI.[10] Different results were obtained with 1 (R = $OC_{10}H_{21}$) in which the cross-coupling step was found to be very sensitive to the amount of CuI. In this case we isolated only trace amounts of the monoacetylene coupling product under conditions of catalytic CuI. However, if the reaction is performed with stoichiometric CuI and catalytic (5%) $(Ph_3P)_2PdCl_2$, the coupling product is obtained in 88% yield. Cuprous acetylides are well known to displace aromatic iodides,[11] but this reaction generally requires temperatures around 100 °C. We have discounted the possibility that the cuprous acetylidene may be reacting directly with the aryl iodide by conducting control experiments which excluded palladium. Under these conditions we generated no detectable product. However, it still seems likely that the dramatic increase in yield is due to a higher concentration of the cuprous acetylide present in the reaction mixture. A higher concentration of this reactive species would result in a more efficient transmetalation of the $(Ph_3P)_2PdAr(I)$ intermediates formed by the oxidative addition of $(Ph_3P)_2$-Pd to the aromatic iodides.[10] Oxidative additions are known to be reversible reactions.[12] As a result, a plausible explanation is that $(Ph_3P)_2PdAr(I)$ is present only in low concentration due to a reversible oxidative addition step with an unfavorable equilibrium constant. We have observed similar results with other electron-rich aromatic iodides[13] and are studying this effect further to confirm its origin.

The diacetylene linkages were formed by oxidative coupling with the Hay catalyst.[14,15] Macrocyclic diacetylenes **2**, **3**, and **4** can be synthesized by one-pot oxidative coupling of **1** (Scheme 1), or by a multistep synthesis whereby diacetylene linkages are formed in two steps (Scheme 2). The stepwise synthesis of diacetylenes has the advantage that only macrocycles containing an even number of phenyl rings can be produced.

As summarized in Scheme 1, the one-pot oxidative coupling procedure of **1** produces useful amounts of macrocyclic products in addition to diacetylene polymer if the reaction is performed under fairly dilute conditions (Table 1). The macrocyclic products are readily separated from the polymers by silica gel chromatography. Compound **2** (R = $C_{10}H_{21}$, $OC_{10}H_{21}$, $C_{12}H_{25}$) is conveniently isolated from the larger macrocycles by fractional recrystallization, whereas the shorter side-chain derivatives and all derivatives of **3** and **4** require a combination of fractional recrystallization and chromatography.

The efficiency of the cyclization reaction is most likely a result of the high rigidity of **1**. The structures of **2** and **3** are assigned on the basis of correlations between mass spectroscopic and ^1H NMR data. Compound **2** (R = H) had been previously isolated and its structure was deter-

(10) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(11) (a) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. (b) Sladkov, A. M.; Gol'ding, I. R. *Russ. Chem. Rev.* **1979**, *48*, 868.

(12) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(13) For example: *N,N,N',N'*-tetramethyl-2,5-diamino-1-iodobenzene gave no detectable cross-coupling products with catalytic Pd and CuI. However, with 1 equiv of CuI and catalytic Pd we obtained a 70% yield of the coupling product with (trimethylsilyl)acetylene.

(14) Macrocycle **2** with R = H has been previously reported. (a) Behr, O. M.; Eglinton, G.; Raphael, R. A. *Chem. Ind.* **1959**, 699. (b) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614.

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Table 1. Yields of Diacetylene Macrocycles

R	yield[a] % 2	3	4
H	35[b]		
C_4H_9	31[b]	21[b]	9[b]
C_6H_{13}	30[b]	19[b]	8[b]
	13[b,d]		45[b,d]
	11[b,e]	14[b,e]	5[b,e]
	20[c,e]	45[c,e]	
$C_{10}H_{21}$	74[c]	9[b]	9[b]
$C_{12}H_{23}$	54[c]	15[b]	16[b]
	16[b,e]	19[b,e]	5[b,e]
$OC_{10}H_{21}$	17[c]	33[b]	26[b]

[a] Unless stated otherwise all yields are for the procedure in Scheme 1 and method A. [b] Isolated as a mixture of macrocycles and the relative amounts were determined by NMR. [c] Isolated recrystallized yield. [d] Produced by stepwise synthesis, Scheme 2. [e] Yield from Method B. **Method A**: a mixture of 1 (0.025 M) and 1.1 equiv of CuCl in *o*-dichlorobenzene was saturated with O_2 by continuous bubbling and then a large excess (23 equiv) of TMEDA was added. **Method B**: an *o*-dichlorobenzene solution of 1 (0.014 M) was added dropwise over 20 min to an oxygen-saturated solution containing 1.1 equiv of CuCl (0.014 M) in *o*-dichlorobenzene and 23 equiv of TMEDA.

mined by chemical methods.[14] Although mass spectroscopic data could not be obtained for all of the derivatives of 2 and 3 due to high molecular weight and/or chemical instability, the structures may be unambiguously assigned due to clear ^{1}H NMR correlations with homologues which were confirmed by mass spectroscopy. The downfield region of ^{1}H NMR is particularly diagnostic, and the R = alkyl derivatives of 2 and 3 exhibit aromatic resonances at δ 6.73 and 7.41 ($CDCl_3$), respectively. Similarly, the R = $OC_{10}H_{21}$ derivatives display peaks of δ 6.37 and 7.08 ($CDCl_3$) which we assign to 2 and 3, respectively. The strained dimeric macrocycles 2 are also readily distinguishable by their yellow color. Complete characterization of the tetrameric macrocycles 4 proved problematic and these compounds were prone to decomposition. We were unable to obtain mass spectral analysis of any of the derivatives of 4 as a result of their high molecular weight and reactivity. Our attempts to transform 4 into a more stable compound by hydrogenating the acetylene linkages gave very complex mixtures of compounds. However, after 2 and 3, the compound assigned to structure 4 is the next most abundant macrocycle produced in the reaction mixture. Additionally, this compound is the dominant product in the stepwise synthetic procedure (Scheme 2), thereby indicating that it contains an even number of phenyl rings. Since similar macrocyclic structures have been previously isolated,[16] we have no reason to believe that compound 4 would not be present. Hence, on the basis of the available data we conclude that the compounds assigned structure 4 are the cyclic tetramers. Again, ^{1}H NMR is very diagnostic within a homologous series and the R = alkyl derivatives of 4 exhibit a single aromatic resonance at δ 7.29. The R = $OC_{10}H_{21}$ derivative exhibits an aromatic resonance at δ 6.93. It is also noteworthy that these resonances are just downfield of the polymeric material which displays broad aromatic signals at $\delta \approx 7.2$ and 6.9 for R = C_6H_{13} and $OC_{10}H_{21}$, respectively. Hence, the large upfield shift observed for the aromatic resonances in going from 3 to 4 is likely an indication that 4 exhibits a less constrained conformation which more closely resembles that of the polymer.

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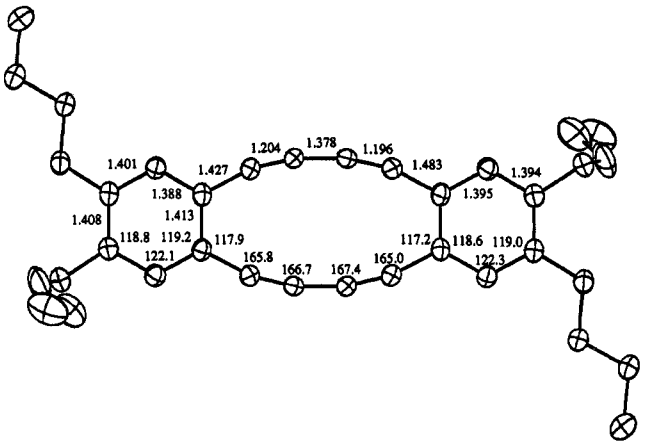


Figure 1. ORTEP of 2 (R = C_4H_9) showing selected bond lengths on top and the bond angles on bottom.

The diacetylene cyclization reaction is extremely sensitive to the conditions employed, and we found that the yields often varied with changes in the reaction scales. The best conditions studied involved short reaction times (30 min) obtained with method A as detailed in Table 1. This procedure gave reproducible yields in small-scale reactions (ca. 0.1 g), allowing for the determination of the product trends, and gave qualitatively similar yields in preparative reactions. We also found that the relative amounts of 2, 3, and 4 vary with the length of the alkyl groups (Table 1). Shorter side chains (R = C_4H_9, C_6H_{13}) gave reaction mixtures with greater amounts of larger macrocycles and polymers relative to the longer side-chain derivatives (R = $C_{10}H_{21}$, $C_{12}H_{25}$), which gave high yields of the smaller macrocycles. This effect is not of electronic origin and is likely a result of decreased mobility associated with larger side chains. Decreased mobility favors intramolecular cyclizations of acyclic diacetylene intermediates since intermolecular coupling requires interdiffusion of reactive fragments. The strongly electron donating R = $OC_{10}H_{21}$ group appears to favor the formation of larger macrocycles. We do not believe that the R = $OC_{10}H_{21}$ group destabilizes the smaller macrocycles; more likely it reflects other factors such as changes in conformational preferences, the rate of formation of the reactive intermediates, and/or solvent interactions.

We considered 2 to be particularly interesting due to its highly strained structure. As a result, we endeavored to increase the yields of this dimeric macrocycle by conducting the Hay coupling under more dilute conditions and longer reaction times (6 h). However, we found that slow addition of 1 to dilute catalyst solutions (method B, Table I) resulted in lower apparent yields of 2 and unidentifiable polymeric products. A plausible explanation of this result is that the reactive intermediates, presumed to be acetylenic radicals,[17] are reacting with 2 to produce complex polymeric products. We note that others have also reported improved yields in similar diacetylene cyclization reactions with shorter reaction times.[15a] In search of a higher yield and more convenient synthesis of shorter side-chain derivatives of 2 which may be efficient under dilute conditions, we investigated a stepwise synthesis of 2 (R = C_6H_{13}) whereby an acyclic precursor (6) is isolated and then cyclized in dilute solution

(17) Clifford, A. A.; Waters, W. A. *J. Chem. Soc.* **1963**, 3056.

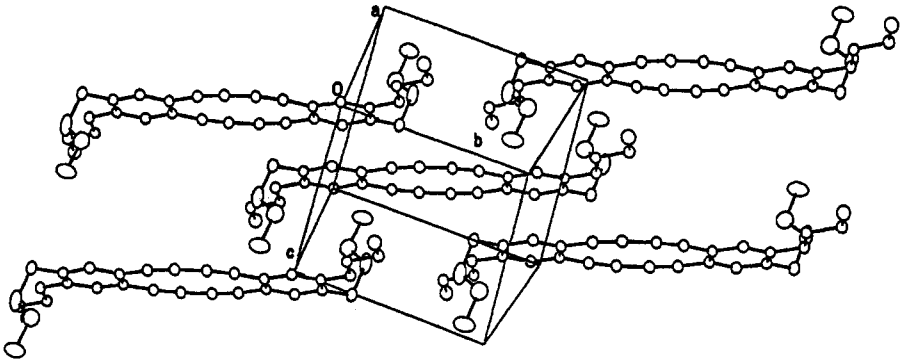


Figure 2. ORTEP of 2 (R = C_4H_9) showing the unit cell. The space group is triclinic with a = 7.222, b = 9.334, and c = 11.012 Å, α = 108.59°, β = 105.67°, and γ = 96.10°.

(Scheme 2).[18] This synthesis is conveniently employed due to the chemoselectivity of the cross-coupling reaction to produce the monoacetylene product **5**. Unfortunately, after investigation of the ring closure of **6** with a number of conditions, we have found that it is in fact less effective for the preparation of **2** than the simpler one-pot procedure in Scheme 1. However, we have found that **4** (R = C_6H_{13}) can be produced in 45% yield by this route, thereby providing a more effective route to this compound than by the one-pot procedure in Scheme 1, which gave **4** in 8%.

We considered that **2**'s strained structure could impart unique diacetylene reactivity from which novel topochemical polymerizations may be developed. To better understand **2**, an X-ray crystal structure of the R = C_4H_9 derivative was performed.[26] Figures 1 and 2 show the unsaturated portion of the molecule to be planar and the bond angle deformations imposed by the cyclic structure to be localized in the acetylenic groups. The bond angles about the acetylene carbons are distorted by 13–15° away from a 180° strain-free geometry, whereas the connections to the benzene are distorted by only 2–3°. The alkyl chains with the out-of-plane conformations exhibit large thermal parameters compared to the in-plane side chains.

We have also investigated the solid-state polymerizations of **2**. Previous investigations of topochemical polymerizations of the cyclic diacetylenes with comparatively low ring strain concluded that the solid-state packing was more important than ring strain effects.[8] The high reactivity of **2** is readily apparent, and its crystals spontaneously polymerize at 100–125 °C. The R groups also influence **2**'s stability, and when R = H the compound can only be handled for brief periods at room temperature without problematic decomposition.[14,19] The other derivatives which contain electron-donating alkyl and alkoxy groups can be stored as solids at room temperatures for a few days with only minor decomposition. In addition, we have made numerous unsuccessful attempts to isolate electron-poor phthalic ester and phthalic imide derivatives of **2**; hence it appears that **2** is stabilized by electron-donating groups. The thermally induced exothermic polymerization has been studied by differential scanning calorimetry (DSC) and two representative examples are shown in Figure 3. The sharp nature of the large exothermic transitions ($w^{1/2}$ = 1.4–1.5 °C) is indicative of a chain

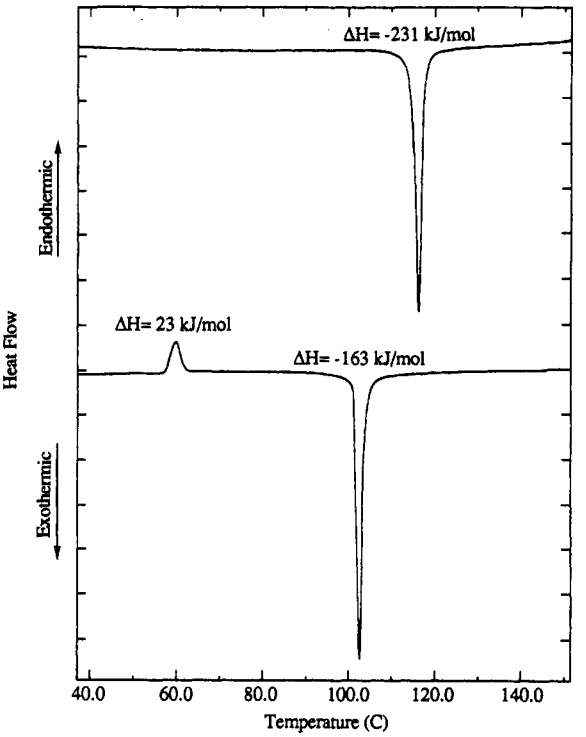


Figure 3. Representative DSC thermograms of **2** (R = C_6H_{13}, 2 °C/min, top; R = $C_{10}H_{21}$, 20 °C/min, bottom) showing the large exothermic polymerization transition and an additional crystal-to-crystal transition for R = $C_{10}H_{21}$.

reaction, and integration of the enthalpies shows different polymerization enthalpies per diacetylene for different R groups. This effect is an indication that the crystal packing is influencing the nature of the polymerizations. Topological polymerizations of acyclic crystalline diacetylenes have been reported to give values of 150–165 kJ/mol.[5] As shown in Figure 3 for the R = $C_{10}H_{21}$ derivative, longer side chains produce additional endothermic crystal-to-crystal phase transitions prior to polymerization. Although these types of transitions are often found in materials which are thermotropic liquid crystals at higher temperatures, none of these compounds were found to be liquid crystalline. The polymers were characterized by a number of methods. X-ray powder diffraction showed that the polymers derived from **2** exhibit lamellar arrangements, which was expected as a result of their structure and the long flexible side chains. However, the structures obtained to date are sufficiently disordered such that further structural analysis has not been possible. IR spectroscopy showed no evidence of acetylene linkages after polymer-

(18) Stepwise procedures have recently been shown to be very effective in the selective synthesis of macrocycles with palladium cross-coupling reactions. Moore, J. S.; Zhang, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 922.

(19) The authors in ref 14 report that **2** (R = H) explodes with heating.

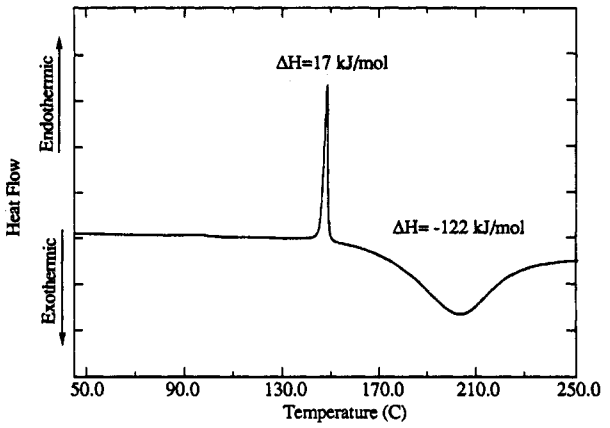
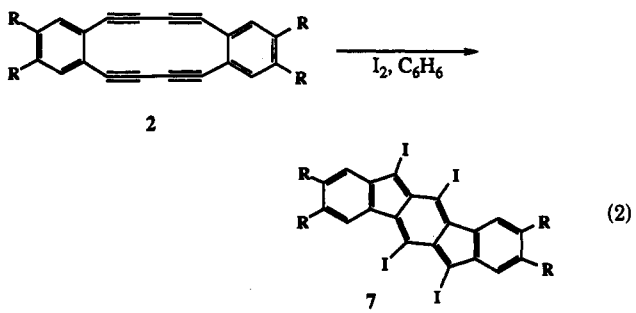


Figure 4. DSC of **3** (R = C_6H_{13}, 20 °C/min) showing an endothermic melting transition followed by a broad exothermic polymerization.

ization, indicating that this material does not undergo a typical diacetylene polymerization. Solid-state CP-MAS ^{13}C NMR was ineffective in determining the polymer's structure due to a high concentration of carbon-centered radicals. The polymers exhibit a very strong ESR signal. These results indicate that **2** does not appear to undergo a well-defined topochemical polymerization. The lack of specificity in these polymerizations and the intractable nature of the products preclude further characterization of the nature of the polymerization for the derivatives in hand. However, the spontaneous nature of **2**'s polymerization is promising and given the proper orientation in a crystal it can likely be made to exhibit a topochemical polymerization.

In contrast to **2**, we find that compounds **3** are thermally robust and polymerize to give intractable dark brown materials at higher temperatures (ca. 200 °C) in a molten isotropic state. This process can be monitored by DSC (Figure 4) and a typical behavior is shown for **3** (R = C_6H_{13}), which undergoes a endothermic melting transition followed by a very broad exothermic transition ($w^{1/2} \approx 30$ °C) associated with a transition to a dark brown polymeric substance. The polymerization enthalpy is less than typical topochemical diacetylene polymerizations, and the broad nature of the polymerization exotherm indicates that a very random polymerization reaction occurs. Due to the lack of interesting behavior, we have not studied these polymerizations further.

In an effort to better understand the reactivity of **2** in solid-state polymerizations, we have examined its chemical reactions in solution. The close proximity of the diacetylene linkages suggests that intramolecular cyclization reactions may dominate the reactivity of **2**. Other cyclic diacetylene and annulene compounds in which non-proton-bearing carbons are proximal have been reported to undergo facile cyclizations to produce biradical species.[20-23] Additionally, in Eglinton's original studies of **2** (R = H), it was found that reductive hydrogenation with Na/NH_3 resulted in intramolecular cyclization to produce a 6-5-6-5-6 fused ring system.[14] Indeed, we find evidence for related processes and reaction of **2** with iodine in benzene (eq 2) results in the formation of an air-sensitive purple compound with limited solubility. IR indicates that the product no longer contains acetylene groups. This compound is assigned structure **7** on the basis of a ^1H NMR spectrum, which displays two single aromatic signals, HRMS, and elemental analysis. The limited solubility of **7** required ^{13}C NMR to be performed in C_6D_6 at elevated temperature, which only revealed nine of the expected ten sp^2 carbon resonances. We believe the missing resonance is obscured by the solvent. The ring system of **7** contains the same 6-5-6-5-6 fused ring architecture produced by Eglinton. This reaction is general and is observed for all of the derivatives of **2** with isolated yields of 50–67%. These reactions proceed to completion in 1.5 h at rt, conditions under which all but the R = H derivative are stable, thus indicating that the reaction is not zero order in iodine. The yields of **7** were found to be much lower when the solvent was toluene, suggesting that radical intermediates may be involved. However, trapping reactions with a variety of hydrogen atom donors and radical acceptors have not yielded characterizable products. Therefore, the presence of radical intermediates in this reaction is uncertain.



Compounds with structure **7** are relatively stable in the solid state; however solutions of these 20π electron system are oxidized under aerobic conditions in about 10 to 20 min to produce red compounds as the sole observable products. The IR of these products indicate the presence of a ketone, ^1H NMR displays two aromatic singlets, and ^{13}C NMR displays ten sp^2 carbons. This information and further characterization of these products by HRMS and elemental analysis indicates that these compounds have structure **8** in which two of the iodides of **7** have been replaced by oxygens. As shown in Scheme 3, we considered that **8** may be produced either by the result of direct reaction of **7** with O_2 or the result of hydrolysis of **7** to produce a diol which is then oxidized. We considered the latter possibility to be most likely since nucleophilic attack at the iodine-bearing carbon of the five-membered ring would generate an aromatic anionic intermediate. However, when the reaction is conducted in the presence of $^{18}OH_2$, ^{18}O was not incorporated into **8** and addition of dry oxygen to **7** produced **8** quantitatively. Hence, we conclude that the source of the carbonyl oxygen is O_2, suggesting that **8** results from direct oxidation of **7**.

Conclusion

We have reported procedures for the synthesis of a family of macrocyclic diacetylenes in useful quantities. Although the compounds reported are not thermotropic liquid crystals, further extensions of this chemistry should allow

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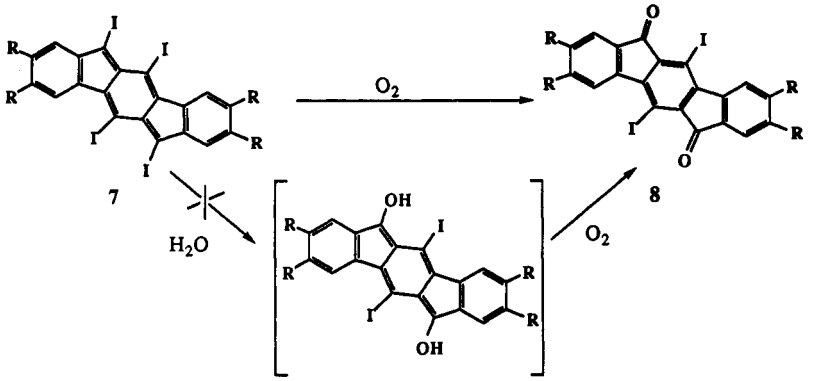
(23) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986.

Scheme 3



for the synthesis of diacetylene liquid crystals which are attractive precursors for the synthesis of new polymers. In this regard, columnar liquid crystals of the larger macrocycles **3** and **4** may be routes to new polymeric tubular structures. The strained cyclic structure of **2** imparts interesting reactivity with a pronounced tendency to undergo intramolecular cyclization reactions. This reactivity has provided a new synthetic route to new polycyclic structures **7** and **8**. We are currently exploring the synthesis and solid-state polymerizations of a number of derivatives of **2** in an effort to develop new well-defined polymers. The possibility presented by **2** of a simultaneous intramolecular cyclization and topochemical polymerization is a promising method by which to prepare novel all-carbon ladder polymers.[9]

Experimental Section

General. All chemicals were of reagent grade. Diisopropylamine was predried over NaOH and vacuum distilled. THF, ether, and toluene were vacuum distilled from sodium benzophenone ketyl and stored in Teflon sealed flasks under argon. All other solvents were used without purification. TMEDA is *N,N,N′,N′*-tetramethylethylenediamine. NMR spectra were recorded on Bruker 250- or 500-MHz spectrometers in $CDCl_3$ or C_6D_6. Chemical shifts are reported in ppm using $CHCl_3$ or C_6HD_5 as an internal reference. Mass spectroscopy was performed using $CHCl_3$ as solvent on a VG analytical ZAB-E instrument; FAB spectra were measured in a 3-nitrobenzyl alcohol matrix. Chromatography was performed on 40 μm silica gel (Baker). IR spectra were obtained with a Perkin-Elmer 1760-X FT-IR spectrometer. The DSC data were taken on a Perkin-Elmer DSC-7.

1,2-Dihexylbenzene (General Procedure for 1,2-Dialkylbenzenes). A flame-dried, 1-L, round-bottom flask was charged with Mg chips (13.8 g, 0.575 mol) under an argon atmosphere, an ether solution of 1-bromohexane (79.9 mL, 0.569 mol) was added, and a small amount of I_2 was added to initiate the reaction. The addition of 1-bromohexane was adjusted to maintain a constant reflux. The reaction mixture was cooled to room temperature and filtered under an inert atmosphere to remove any unreacted Mg metal. (1,3-Bis(diphenylphosphino)propane)-nickel(II) chloride (0.7 g, 1.29 mmol) was then added in portions while 1,2-dichlorobenzene (32.12 mL in 70 mL of ether) was added dropwise. The reaction mixture turned dark brown with heavy MgBrCl precipitates. This mixture was refluxed for 1.5 h and then cooled to rt and poured into 320 mL of a 6 M H_2SO_4 solution with ice. The ether layer was separated and washed several times with 3 M H_2SO_4, H_2O, $NaHCO_3$, and H_2O and dried over $MgSO_4$. The solvent was removed under vacuum, and the resultant oil was chromatographed through silica gel with a minimum amount of hexane. The low-boiling components were distilled off to give pure 1,2-dihexylbenzene at 245 °C/6 mmHg as a colorless liquid (colorless oil, lit.[24]) (55 g, 78.6%): ^1H NMR ($CDCl_3$) 0.84 (t, J = 6.3 Hz, 6H), 1.20–1.70 (m, 16H), 2.54 (t, J = 7.7 Hz, 4H), 7.02–7.18 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$) 14.11, 22.66, 29.51, 31.33, 31.80, 32.72, 125.70, 129.10, 140.57 ppm; IR (neat) 3021, 2950, 2922, 2860, 1493, 1471, 1379, 1049, 719 cm^{-1}; MS m/z (rel intensity) 246 (M^+, 100), 175; HRMS calcd for $C_{18}H_{30}$ (M^+) 246.2347, found 246.2335.

4,5-Dihexyl-1,2-diiodobenzene (General Procedure for 4,5-Dialkyl-1,2-diiodobenzene). 1,2-Dihexylbenzene (10 g, 0.0406 mol) was added to a mixture of glacial acetic acid (150 mL), H_2SO_4 (concd, 9.0 mL), H_2O (1 mL), $NaIO_3$ (4.016 g, 20.3 mmol), and I_2 (11.34 g, 44.7 mmol). After the mixture was refluxed overnight, a saturated aqueous $Na_2S_2O_4$ solution was added until the color of the mixture changed from purple to light brown. The mixture was extracted with CH_2Cl_2, washed with saturated $Na_2S_2O_4$, H_2O, and brine, and then dried over K_2CO_3. Removal of the solvent by vacuum gave a brownish residue which was redissolved in acetone and decolorized with activated carbon. White crystals (8.97 g, 44.4%) were collected: mp 30.1–31.8 °C; ^1H NMR ($CDCl_3$) 0.88 (t, J = 6.2 Hz, 6H), 1.17–1.65 (m, 16H), 2.48 (t, J = 7.6 Hz, 4H), 7.59 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.06, 22.54, 29.23, 30.84, 31.74, 31.89, 104.02, 139.73, 142.66 ppm; IR (KBr) 3035, 2964, 2936, 2865, 1757, 1567, 1461, 1142, 1113, 890, 868, 727, 642 cm^{-1}; MS m/z (rel intensity) 498 (M^+), 404, 372, 256, 192, 160 (100), 137, 128; HRMS calcd for $C_{18}H_{28}I_2$ (M^+) 498.0280, found 498.0271. Anal. Calcd for $C_{18}H_{28}I_2$: C, 43.37; H, 5.67. Found, C, 43.24; H, 5.66. For R = C_4H_9, colorless oil (58.1%); R = $C_{10}H_{21}$, white crystals (51.0%); mp 33.5–35 0 °C; R = $C_{12}H_{25}$, white crystals (44.5%); mp 43.5–45.5 °C.

4,5-Dihexyl-1,2-diethynylbenzene (General Procedure for 1, R = alkyl). Under an atmosphere of argon, 4,5-dihexyl-1,2-diiodobenzene (8.08 g, 16.2 mmol), CuI (77 mg, 0.40 mmol), and $Cl_2Pd(PPh_3)_2$ (280 mg, 0.40 mmol) were mixed in diisopropylamine (200 mL). (Trimethylsilyl)acetylene (5.0 mL, 35.6 mmol) was then added dropwise, and the reaction mixture turned brown with heavy precipitates. The mixture was stirred overnight at rt and the solvent was removed by vacuum. The residue was chromatographed on a 3 × 7 cm column of silica gel (CH_2Cl_2/hexane, 1/10) to give 4,5-dihexyl-1,2-bis((trimethylsilyl)ethynyl)-benzene as a colorless oil (7.04 g, 99.1%): ^1H NMR ($CDCl_3$) 0.26 (s, 18H), 0.88 (t, J = 6.3 Hz, 6H), 1.16–1.60 (m, 16H), 2.51 (t, J = 7.7 Hz, 4H), 7.22 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 0.13, 14.13, 22.71, 29.37, 30.59, 31.91, 32.42, 96.33, 103.73, 122.95, 132.90, 141.31 ppm. For R = H, yellow oil (80%), ^1H NMR ($CDCl_3$) 0.26 (s, 18H), 7.18–7.24 (m, 2H), 7.42–7.49 (m, 2H) ppm; R = C_4H_9, yellow oil (76%); R = $C_{10}H_{21}$, colorless oil (90%); R = $C_{12}H_{25}$, colorless oil (92%). 4,5-Dihexyl-1,2-bis((trimethylsilyl)ethynyl)-benzene (7.04 g, 16.1 mmol) was dissolved in a mixture of THF (20 mL) and CH_3OH (100 mL). A KOH solution (2 pellets in 2 mL of H_2O) was then added, and after stirring overnight at rt, the reaction mixture was added to H_2O (100 mL) and the pH was adjusted to 7 with HCl. The product was extracted with CH_2Cl_2 and washed with brine and H_2O and dried over $MgSO_4$. The solvent was removed by vacuum and the product was chromatographed on a 3 × 7 cm column of silica gel (CH_2Cl_2/hexane, 1/8)

(24) Areshidze, K. I.; Shetsiruli, G. I. *Izv. Akad. Nauk. Gruz. SSR. Ser. Khim.* **1986**, *12*(3), 237–40; *Chem. Abstr.* **1982**, *106*, 175868Y.

to give 1 (R = C_6H_{13}) as a yellow oil (4.73 g, 100%): ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 6.3 Hz, 6H), 1.10–1.65 (m, 16H), 2.54 (t, J = 7.7 Hz, 4H), 3.25 (s, 2H), 7.26 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 13.99, 22.66, 29.46, 30.80, 32.03, 32.95, 79.85, 82.23, 122.11, 133.21, 141.73 ppm; IR (neat) 3305, 3071, 2957, 2929, 2858, 2106, 1571, 1493, 1457, 1436, 1252, 1124, 1032, 748, 656 cm^{-1}; MS m/z (rel intensity) 295 (M^+ + 1, 100), 271, 220, 153; HRMS calcd for $C_{22}H_{31}$ (M^+ + 1) 295.2426, found 295.2433. For R = H, colorless oil (90%): ^{1}H NMR ($CDCl_3$) 3.35 (s, 2H) (lit.[25] 3.37 ppm), 7.24–7.34 (m, 2H), 7.46–7.56 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$) 81.13, 81.77, 124.99, 128.47, 132.58 ppm; IR (neat) 3291 (lit.[25] 3300 cm^{-1}), 2106 (lit.[25] 2070 cm^{-1}), 1471, 1440, 1265, 1244, 1095, 954, 759, 666, 631 cm^{-1}; MS m/z (rel intensity) 126 (M^+, 100); HRMS calcd for $C_{10}H_6$ (M^+) 126.0469, found 126.0472. R = C_4H_9, colorless liquid (100%). R = $C_{10}H_{21}$, colorless liquid (100%). R = $C_{12}H_{25}$, colorless liquid (100%).

4,5-Didecenoxy-1,2-diiodobenzene. To a solution of 1,2-didecenoxybenzene (2.00 g, 5.13 mmol) in CH_2Cl_2 (70 mL) was added mercuric acetate (3.26 g, 10.23 mmol) followed by dropwise addition of iodine (2.50 g, 10.26 mmol) in CH_2Cl_2 (20 mL) over 0.5 h. The reaction mixture was stirred at rt for 4 h and then filtered through Celite 545. The insoluble salts were then rinsed with additional quantities of CH_2Cl_2 (2 × 20 mL). The filtrate was washed with $Na_2S_2O_4$, $NaHCO_3$ (saturated), H_2O, brine, and H_2O and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was recrystallized from ethanol to give colorless plate crystals (2.69 g, 81.8%): mp 45.6–47.2 °C; ^{1}H NMR ($CDCl_3$) 0.89 (t, J = 6.1 Hz, 6 H), 1.05–1.50 (m, 28H), 1.77 (m, 4H), 3.91 (t, J = 6.2 Hz, 4H), 7.22 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.10, 22.63, 25.86, 27.18, 28.98, 29.28, 29.53 (2C), 31.85, 69.32, 95.96, 123.58, 149.61 ppm; IR (KBr) 3092, 3063, 2950, 2907, 2850, 1574, 1489, 1468, 1333, 1241, 1191, 1014, 858, 716, 631 cm^{-1}; MS m/z (rel intensity) 642 (M^+), 534, 516, 390, 376, 291, 252, 236, 141, 108 (100); HRMS calcd for $C_{26}H_{44}O_2I_2$ (M^+) 642.1430, found 642.1453. Anal. Calcd for $C_{26}H_{44}O_2I_2$: C, 48.59; H, 6.91. Found: C, 48.74; H, 7.09.

1,2-Didecenoxy-4,5-diethynylbenzene (1, R = $OC_{10}H_{21}$). This compound was prepared by the same procedure given above for R = C_6H_{13} except that 2 equiv of CuI was used and the reaction mixture was stirred at 70 °C for 14 h. The TMS-protected compound was obtained as a yellow oil (88%): ^{1}H NMR ($CDCl_3$) 0.21 (s, 18H), 0.83 (t, J = 7.5 Hz, 6H), 1.10–1.58 (m, 28H), 1.75 (m, 4H), 3.92 (t, J = 7.6 Hz, 4H), 6.84 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 0.11, 14.09, 22.66, 25.92, 29.04, 29.33 (2C), 29.55 (2C), 31.89, 69.06, 96.38, 103.61, 116.16, 118.68, 143.04 ppm. Deprotection gave 1 (R = $OC_{10}H_{21}$) (73.2%): mp 52.0–53.8 °C; IR (KBr) 3298, 3255, 3085, 2929, 2844, 2595, 2106, 1716, 1507, 1337, 1259, 1010, 698, 669, 592 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.4 Hz, 6H), 1.05–1.50 (m, 28H), 1.75 (m, 4H), 3.24 (s, 2H), 3.96 (t, J = 7.5 Hz, 4H), 6.84 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.06, 22.63, 25.54, 25.87, 28.95, 29.30 (2C), 29.53, 31.86, 69.06, 79.35, 82.12, 116.40, 117.70, 149.28 ppm; MS m/z (rel intensity) 439 (M^+ +1, 100), 298, 158; HRMS calcd for $C_{30}H_{47}O_2$ (M^+ +1) 439.3576, found 439.3562. Anal. Calcd for $C_{30}H_{46}O_2$: C, 82.13; H, 10.58. Found: C, 81.86; H, 10.76.

Cyclization of 1 (R = $C_{12}H_{25}$) by Method A (General Procedure for Formation of Macrocycles 2, 3, and 4). A closed reaction vessel with an O_2 inlet and an oil bubbler outlet was charged with 1,2-dididecyl-4,5-diethynylbenzene (2.0 g, 4.3 mmol), CuCl (0.5 g, 5.1 mmol), and o-dichlorobenzene (175 mL). Oxygen was continuously bubbled through the solution for 15 min to ensure saturation and then TMEDA (15 mL) was added dropwise. The solution mixture immediately turned green and then cloudy brown upon completion of the addition. The mixture was stirred at rt for an additional 30 min at which time TLC showed no starting material. The reaction was quenched by adding 150 mL of 0.5 N HCl to the reaction mixture, and the organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2. The combined organic phases were washed with H_2O, $NaHCO_3$ (saturated) and H_2O, reduced to 30% of the original reaction volume in high vacuum (10^{-4} Torr), and stored at 5 °C overnight to give crude 2 as a yellow powder. Recrystallization from CH_2Cl_2/hexane gave pure 2 (1.06 g, 54%) as yellow needles. The mother liquor was evaporated and the residue was chromatographed on a silica gel column (5 × 5 cm, CH_2Cl_2/hexane, 1/6) to give 0.63 g of a mixture of 3 and 4. The yields of 3 and 4 were 15.4% and 16.1%, respectively, as determined by NMR integration.

Cyclization of 1 (R = C_6H_{13}) by Method B. A 125-mL flask with an O_2 inlet and oil bubbler as an outlet was charged with CuCl (74.5 mg, 0.75 mmol), TMEDA (4.6 mL) and o-dichlorobenzene (50 mL). The solution was saturated with O_2 by continuous bubbling through the solution and then 1,2-dihexyl-4,5-diethnylbenzene (0.2 g, 0.68 mmol) in o-dichlorobenzene (50 mL) was added dropwise over a period of 20 min. The mixture was stirred for 6 h with continuous O_2 bubbling. The same workup detailed in method A was followed. After evaporation of the solvent, silica gel chromatography (26 × 3.0 cm, CH_2Cl_2/hexane, 1/10) gave 2 as yellow needle-like crystals and 3 as white plate crystals with yields of 20% (0.04 g) and 45% (0.09 g), respectively.

Spectral Data of Selected Macrocycles. R = C_6H_{13}. 2: yellow crystals; 113.5 °C dec; ^{1}H NMR ($CDCl_3$) 0.82 (t, J = 7.4 Hz, 12H), 1.05–1.60 (m, 32H), 2.40 (t, J = 7.4 Hz, 8H), 6.73 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$) 14.10, 22.68, 29.60, 30.55, 31.89, 32.38, 83.57, 91.99, 127.88, 129.32, 142.50 ppm; MS m/z (rel intensity) 585 (M^+ + 1, 100), 462, 443, 411, 370; IR (KBr) 2970, 2930, 2865, 2210, 1790, 1535, 1470, 920, 760, 480 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 260.1 (4.54), 273.9 (4.49), 289.7 (4.72), 305.9 (5.02). **3:** mp 146.8 °C; ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.3 Hz, 18H), 1.20–1.68 (m, 48H), 2.58 (t, J = 7.5 Hz, 12H), 7.41 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$) 14.04, 22.57, 29.30, 30.65, 31.67, 32.51, 77.30, 80.82, 122.58, 132.99, 142.18 ppm; MS m/z (rel intensity) 877 (M^+ + 1), 820, 739, 648, 585, 460, 378 (100); IR (KBr) 2960, 2920, 2870, 221, 2150, 1610, 1484, 1450, 1260, 1210, 1020, 900, 850, 800, 700 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 287.8 (4.65), 317.4 (4.91), 339.1 (5.18). Anal. Calcd for $C_{66}H_{84}$: C, 90.34; H, 9.65. Found: C, 90.26; H, 9.94. **4:** ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.3 Hz, 24H), 1.20–1.68 (m, 64H), 2.58 (t, J = 7.5 Hz, 16H), 7.29 (s, 8H) ppm.

R = H. 2: yellow crystals: 78.5 °C dec. ^{1}H NMR ($CDCl_3$) 6.92–6.98 (m, 4H), 7.02–7.08 (m, 4H) ppm.

R = $OC_{10}H_{21}$. 2: yellow orange crystals: 108 °C dec; ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.1 Hz, 12H), 1.13–1.90 (m, 64H), 3.84 (t, J = 7.4 Hz, 8H), 6.37 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$) 14.10, 22.69, 25.88, 28.96, 29.33 (2C), 29.56 (2C), 31.89, 69.12, 83.29, 92.20, 113.52, 123.75, 149.73 ppm; IR (KBr) 2970, 2925, 2110, 1580, 1550, 1500, 1460, 1325, 1275, 1190, 1080, 985, 870, 750, 485 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 290.0 (4.73), 310.0 (4.86). **3:** ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.1 Hz, 18H), 1.13–1.90 (m, 96H), 3.95 (t, J = 7.4 Hz, 12H), 7.08 (s, 6H) ppm. **4:** ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.1 Hz, 24H), 1.13–1.90 (m, 128H), 3.95 (t, J = 7.5 Hz, 16H), 6.93 (s, 8H) ppm.

2-Ethynyl-4,5-dihexyl-1-iodobenzene (5). The same palladium-catalyzed cross-coupling procedure was followed as in the preparation of 1 (R = C_6H_{13}), except that 1.05 equiv of (trimethylsilyl)acetylene was added. Silica gel chromatography with hexane gave pure 2-((trimethylsilyl)ethynyl)-4,5-dihexyl-1-iodobenzene as a colorless oil: ^{1}H NMR ($CDCl_3$) 0.27 (s, 9H), 0.9 (t, J = 7.4 Hz, 6H), 1.17–1.60 (m, 16H), 2.43–2.58 (m, 4H), 7.22 (s, 1H), 7.57 (s, 1H) ppm. Deprotection as described for 1 gave 5, as a colorless oil after chromatography on silica gel with hexane: ^{1}H NMR ($CDCl_3$) 0.89 (t, J = 7.5 Hz, 6H), 1.10–1.60 (m, 16H), 2.37–2.57 (m, 4H), 3.30 (s, 1H), 7.26 (s, 1H), 7.57 (s, 1H) ppm.

2,2′-Diiodo-4,4′,5,5′-tetrahexyldiphenyldiacetylene. The diacetylene coupling reaction of 5 was conducted by method A. After chromatography on silica gel with hexane, 2,2′-diiodo-4,4′,5,5′-tetrahexyldiphenyldiacetylene was isolated as light yellow crystals (62.2%, based upon 4,5-dihexyl-1,2-diiodobenzene): mp 55.8–57.3 °C; ^{1}H NMR ($CDCl_3$) 0.89 (t, J = 7.5 Hz, 12H), 1.10–1.65 (m, 32H), 2.40–2.65 (m, 8H), 7.30 (s, 2H), 7.59 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.07, 22.57, 29.24, 29.30, 30.72, 30.81, 31.64, 32.04, 32.34, 84.26, 97.18, 110.94, 126.23, 134.55, 139.14, 140.87, 114.28 ppm; IR (KBr) 3312, 2957, 2928, 2843, 2149, 1585, 1468, 1362, 1262, 907, 865, 801, 723, 702 cm^{-1}; MS m/z (rel intensity) 790 (M^+, 100), 664, 649, 592, 523, 452, 399, 353; HRMS calcd for $C_{40}H_{56}I_2$ (M^+) 790.2472, found 790.2564.

2,2′-Diethynyl-4,4′,5,5′-tetrahexyldiphenyldiacetylene (6). This preparation followed a similar cross-coupling procedure as was described for 1, except that the mixture was stirred at 70 °C

(25) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* 1980, 627.

overnight to yield the TMS-protected derivative 2,2′-bis((trimethylsilyl)ethynyl)-4,4′,5,5′-tetrahexyldiphenyldiacetylene: ^{1}H NMR ($CDCl_3$) 0.30 (s, 18H), 0.90 (t, J = 7.4 Hz, 12H), 1.10–1.65 (m, 32H), 2.53 (t, J = 7.6 Hz, 8H), 7.24 (s, 2H), 7.26 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 0.04, 14.07, 22.57, 29.19, 29.33, 30.68, 30.80, 31.68, 32.33, 32.48, 81.02, 91.53, 98.09, 103.50, 122.40, 123.88, 132.55, 133.22, 141.32, 141.99 ppm. The procedure of depretection given for 1 was followed to give 6 isolated as light brown crystals. Silica gel chromatography (C_2H_2/hexane, 1/10) gave light yellow crystals in 64.2% yield (based upon 2,2′-diiodo-4,4′,5,5′-tetrahexyldiphenyldiacetylene): mp 40.5–41.5 °C; ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 7.5 Hz, 12H), 1.15–1.70 (m, 32H), 2.54 (t, J = 7.6 Hz, 8H), 3.30 (s, 2H), 7.28 (s, 2H), 7.33 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.27, 22.78, 29.50, 30.93, 31.88, 32.54, 32.66, 78.08, 80.65, 81.15, 82.21, 122.32, 122.85, 133.46, 133.81, 141.96, 142.43 ppm; UV ($CHCl_3$) λ_{max} (log ϵ) 237.4 (4.90), 309.5 (4.36), 331.2 (4.48), 356.9 (4.41); IR (KBr) 3305, 3028, 2957, 2929, 2858, 2135, 2106, 1599, 1486, 1416, 1379, 1202, 904, 868, 727, 642, 606 cm^{-1}; MS m/z (rel intensity) 586 (M^+, 100), 522, 445, 414, 366, 296, 225, 143; HRMS calcd for $C_{44}H_{58}$ (M^+) 586.4539, found 586.4553. Anal. Calcd for $C_{44}H_{58}$: C, 90.03; H, 9.97. Found: C, 89.90; H, 10.21.

7 (R = $C_{12}H_{25}$) (General Procedure). 2 (R = $C_{12}H_{25}$) (0.15 g, 0.163 mmol) was dissolved in benzene (20 mL) in a Schlenk flask under an argon atmosphere. I_2 (0.087 g, 0.34 mmol) was then added and the reaction mixture was stirred at rt for 1.5 h. Purple cotton-like crystals were collected from the reaction mixture (0.15 g, 54.5%): 147 °C dec; ^{1}H NMR (C_6D_6, 500 MHz, 50 °C) 0.82–0.99 (m, 12H), 1.30–1.80 (m, 80H), 2.5–2.7 (m, 8H), 7.35 (s, 2H), 8.69 (s, 2H) ppm; ^{13}C NMR (C_6D_6, 500 MHz, 50 °C, partial) 14.22, 23.05, 29.77, 29.98, 30.09, 30.13, 31.28, 31.50, 32.32, 33.29, 33.69, 94.34, 109.76, 125.75, 136.47, 137.42, 141.97, 142.11, 143.43, 145.72 ppm. IR (KBr) 2963, 2926, 2853, 1518, 1463, 1112, 891, 824, 713 cm^{-1}. Anal. Calcd for $C_{68}H_{104}I_4$: C, 57.12; H, 7.34. Found: C, 57.22; H, 7.70. **R = H.** Dark purple crystals (51.1%), 215 °C dec, which were too insoluble for NMR analysis: MS m/z (rel intensity) 755 ($M^+ - 1$), 629, 534, 409, 307, 254 (100); HRMS calcd for $C_{20}H_8I_4$ (M^+) 755.6805, found 755.6843; IR (KBr) 1521, 1259, 1095, 1025, 805, 755. R = C_4H_9. Purple crystals (67.1%): 215 °C dec; ^{1}H NMR ($CDCl_3$) 0.8–0.95 (m, 12H), 1.15–1.65 (m, 16H), 2.35–2.60 (m, 8H), 7.05 (s, 2H), 8.69 (s, 2H) ppm. MS m/z (rel intensity) 980 (M^+), 953, 909, 854, 813, 759 (100), 734; HRMS calcd for $C_{36}H_{40}I_4$ (M^+) 979.9291, found 979.9363; UV ($CHCl_3$) λ_{max} (log ϵ) 330.2 (4.84), 533.6 (4.65), 571.2 (4.78); IR (KBr) 2957, 2929, 2858, 1514, 1478, 1244, 1109, 1102, 875, 826, 727. Anal. Calcd for $C_{36}H_{40}H_{40}I_4$: C, 44.10; H, 4.08. Found, C, 44.48; H, 4.07.

8 (R = $C_{10}H_{21}$) (General Synthesis from 7). 7 (R = $C_{10}H_{21}$) (150.0 mg, 0.186 mmol) was dissolved in benzene (15 mL) under aerobic conditions, and the solution was stirred at rt for 1 h. After removal of the solvent by vacuum, the residue was recrystallized from CH_2Cl_2/hexane to give 8 (R = $C_{10}H_{21}$) as a red solid (192.6 mg, 95.0%): mp 170 °C; ^{1}H NMR ($CDCl_3$) 0.86 (t, J = 7.5 Hz, 12H), 1.13–1.70 (m, 64H), 2.55–2.76 (m, 8H), 7.46 (s, 2H), 8.78 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$) 14.11, 22.69, 29.34, 29.37, 29.52, 29.62, 29.65, 29.68, 30.62, 30.72, 31.91, 32.57, 33.72, 85.35, 124.15, 125.25, 132.26, 138.81, 139.41, 142.95, 148.27, 149.63, 190.25 ppm. MS m/z (rel intensity) 1095 ($M^+ + 1$), 926, 882, 791, 724, 591 (100); HRMS calcd for $C_{80}H_{87}I_2O_2$ ($M^+ - 1$) 1093.4796, found 1093.4884; IR (KBr) 2950, 2921, 2851, 1712, 1613, 1464, 1407, 1095, 840 cm^{-1}; UV ($CHCl_3$), λ_{max} (log ϵ) 230.5 (4.80), 270.0 (4.58), 317.4 (4.85). Anal. Calcd for $C_{80}H_{88}I_2O_2$: C, 65.78; H, 8.10. Found: C, 65.87; H, 8.35.

8 (R = $C_{12}H_{25}$) (General Synthesis Directly from 2). 2 (R = $C_{12}H_{25}$) (80.0 mg, 0.087 mmol) and I_2 (48.0 mg, 0.19 mmol) were dissolved in benzene (15 mL) under aerobic conditions, and the solution was stirred at rt for 1 h. After removal of the solvent by vacuum, the residue was recrystallized from CH_2Cl_2/hexane to give 8 (R = $C_{12}H_{25}$) as a red solid (64.1 mg, 61.2%): mp 159 °C; ^{1}H NMR ($CDCl_3$) 0.78–1.72 (m, 92H), 2.45–2.70 (m, 8H), 7.44 (s, 2H), 8.77 (s, 2H) ppm; UV ($CHCl_3$) λ_{max} (log ϵ) 233.4 (4.76), 269.0 (4.59), 316.4 (4.93).

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