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Molecular Ribbons via Diels-Alder Cycloadditions: Synthesis of Models for Solubilized Polyacenes and Polyacene Polyquinones

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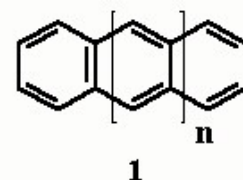
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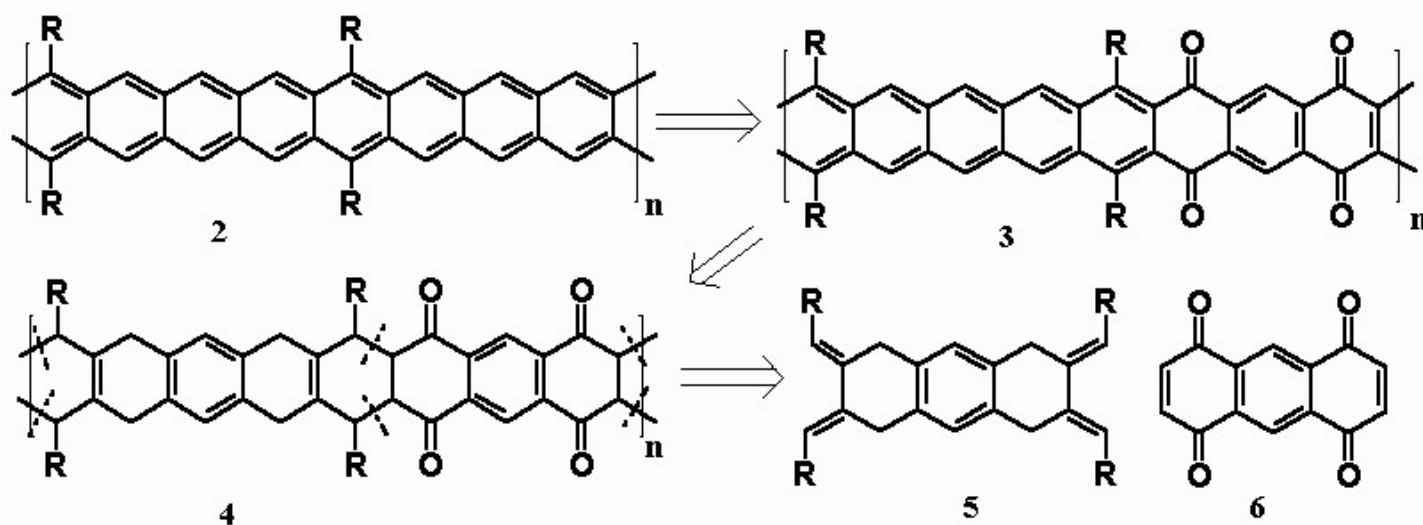
Abstract: Syntheses of linearly fused ribbons of carbocyclic six-membered rings are accomplished by Diels-Alder cycloadditions of a diene (2,3-diheptylidene-1,2,3,4-tetrahydronaphthalene) and a bis-diene (2,3,6,7-tetraheptylidene-1,2,3,4,5,6,7,8-octahydroanthracene) to a bis-dienophile (1,4,5,8-anthraquinone) and a dienophile (1,4-anthraquinone). The Diels-Alder adducts were dehydrogenated to several more highly unsaturated molecular ribbons.

Keywords: Molecular ribbon, Diels-Alder cycloaddition.

The electronic structure of polyacene (**1**), a hypothetical polymer consisting of linearly fused unsaturated six-membered rings, has been of much theoretical interest due to its extended conjugation. For example, Kivelson and Chapman have proposed that this class of materials has the potential to exhibit high temperature superconductivity and ferromagnetism.¹ However, polyacene should be highly insoluble, complicating its purification and handling. The synthesis of a *soluble* polyacene *derivative* would be a highly desirable alternative, since such a polymer might be castable as a thin film.

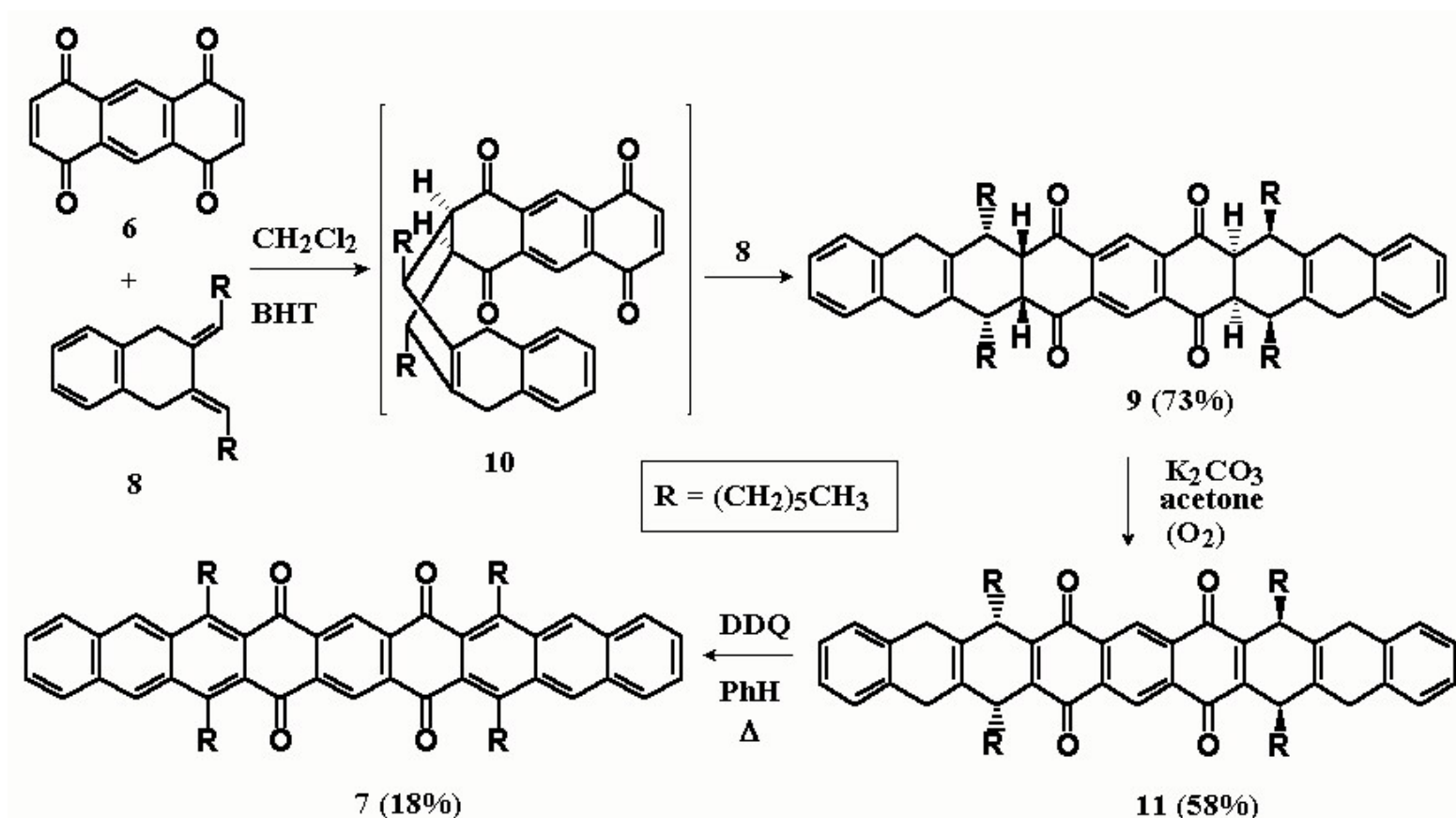


A synthesis of a solubilized polyacene (**2**) is proposed to be accomplished via reductive deoxygenation of polyacene polyquinone **3**, which could be obtained by dehydrogenation of polymer **4**. Polymer **4** could, in turn, be prepared by double Diels-Alder cycloaddition of bis-diene **5** to diquinone **6**.² As a model study for this proposed synthesis, a series of molecular ribbons have been synthesized to qualitatively ascertain the solubilizing ability of hexyl groups in systems related to polyacene.³



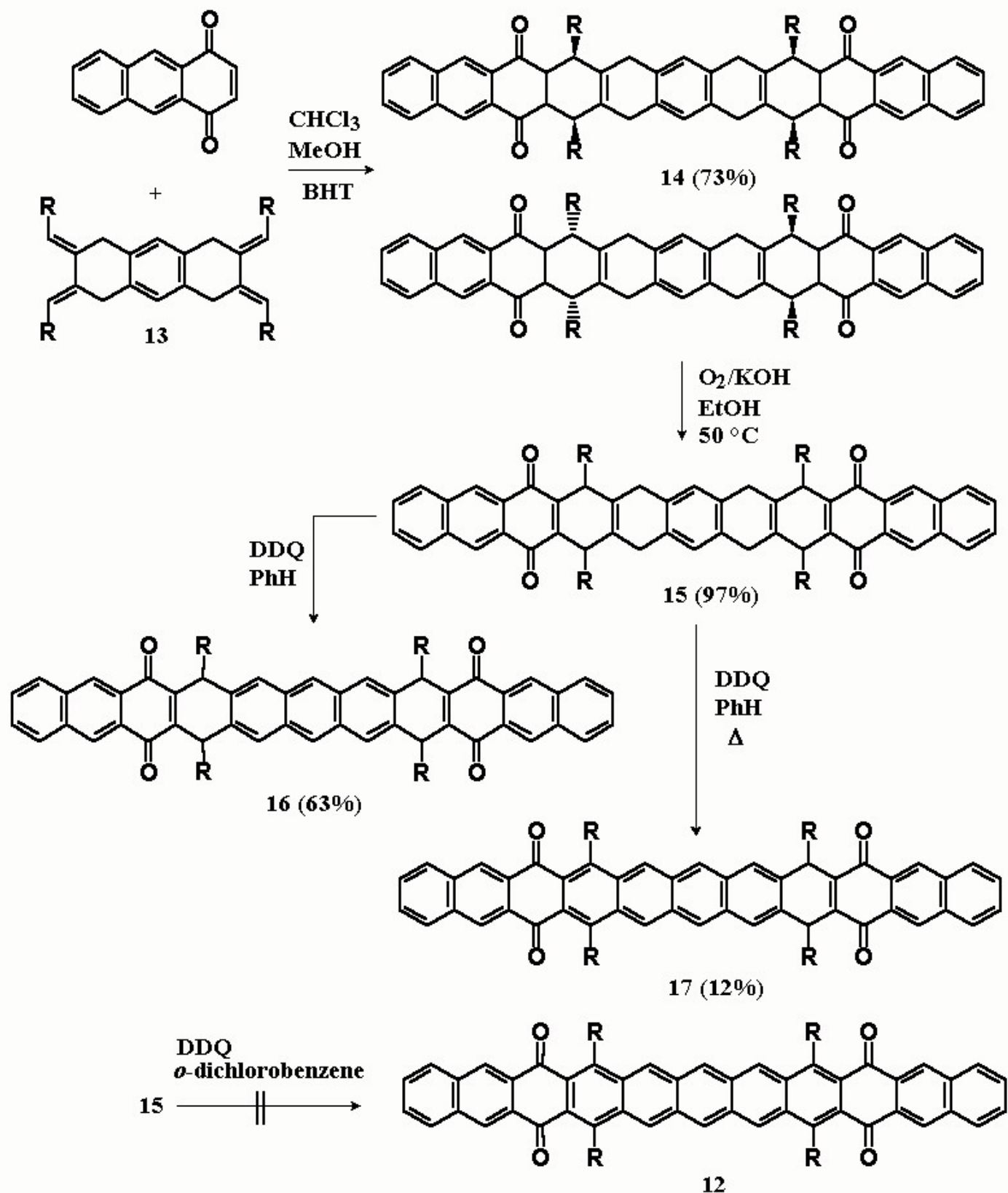
Double Diels-Alder cycloaddition of diene **8**⁴ to diquinone **6**⁴ (in the presence of the anti-oxidant, BHT, to inhibit radical polymerization of the diene) gave adduct **9** in 73% yield, surprisingly as a single stereoisomer. This adduct was assigned a structure consistent with the endo rule for Diels-Alder cycloadditions and with the stereochemistry unambiguously determined for a related adduct.⁵ Furthermore, we believe that it must have resulted from addition of the two diene

molecules to *opposite* sides of the diquinone. Presumably, cycloaddition of diene **8** to diquinone **6** initially gives intermediate monoadduct **10**, although this was not observed. The electron-deficient aromatic moiety in **10** may interact favorably through space with the electron-rich one, thus imparting a preferred U-shaped conformation to the core ribbon structure of the molecule. Addition of diene **8** to monoadduct **10** would then occur preferentially, if not exclusively, to the less hindered face of **10**, resulting in an overwhelmingly predominant formation of the diastereomer shown for **9**.



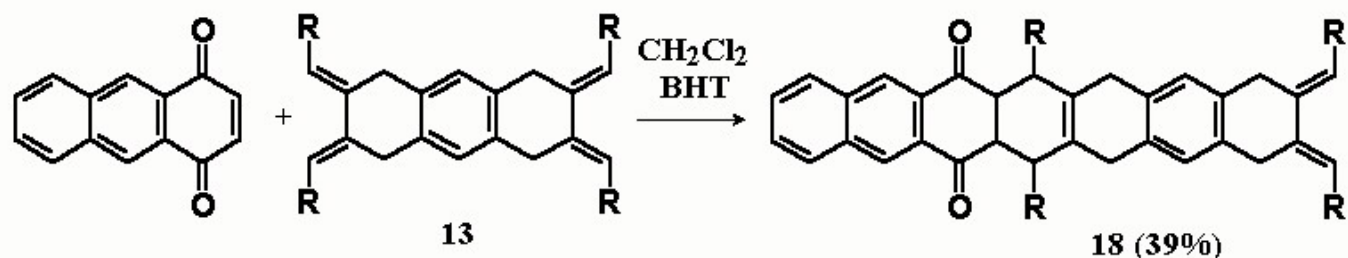
Adduct **9** was treated with potassium carbonate in acetone (in the presence of air in the later stages), giving the double dehydration product, diquinone **11**, in 58% yield. Finally, diquinone **11** was aromatized using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene to give nonacene diquinone **7**, a sparingly soluble brick red solid, in 18% yield.

Similarly, 1,4-anthraquinone underwent cycloaddition to bis-diene **13**⁴ in a refluxing mixture of chloroform and methanol to give 2:1 Diels-Alder adduct **14**, as a mixture of two diastereomers, in 73% yield. Oxidation of **14** in ethanolic potassium hydroxide gave the double dehydrogenation product, diquinone **15**, in 97% yield.

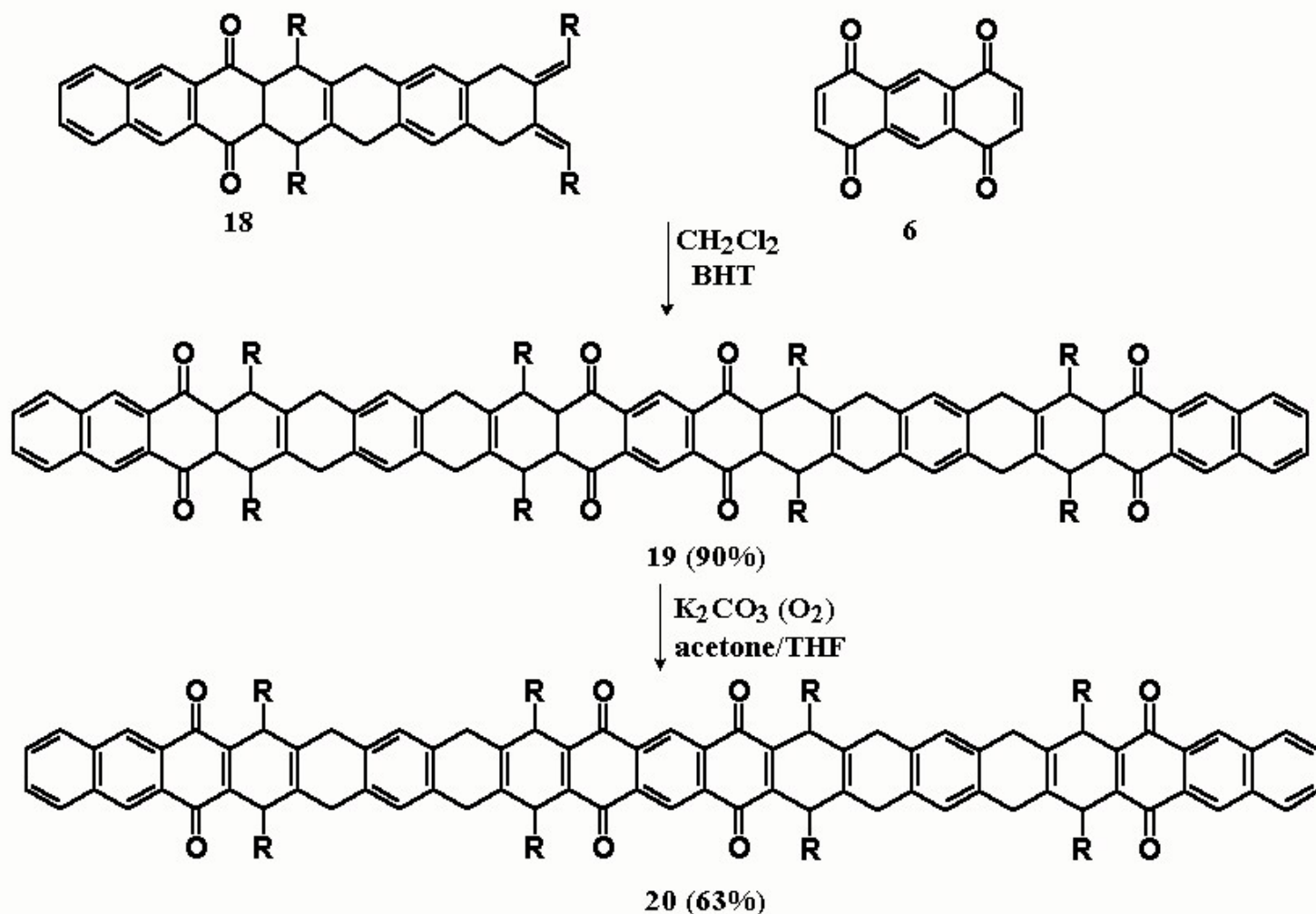


Aromatization of diquinone **15** with DDQ in benzene at room temperature gave anthracene-containing diquinone **16**, while treatment of **15** with DDQ in benzene *at reflux* gave a 68:32 mixture of naphthacene **17** and anthracene **16**, from which a 12% yield of **17** could be obtained. An attempt to produce undecacene diquinone **12** from diquinone **15** by dehydrogenation using DDQ under forcing conditions was not successful.

A molecular ribbon containing nineteen linearly fused carbocyclic six-membered rings was synthesized by first preparing diene **18**, the presumed intermediate in the formation of double adduct **14**, in 39% yield via 1:1 Diels-Alder cycloaddition of bis-diene **13** to 1,4-anthraquinone.



Diene **18** then underwent double cycloaddition to diquinone **6** to give a 90% yield of the desired molecular ribbon, adduct **19**, as a mixture of diastereomers.



This mixture could be smoothly oxidized to tetraquinone **20**, which was also characterized as a diastereomeric mixture.

Conclusions

The Diels-Alder cycloadditions used to synthesize these ribbons of carbocyclic six-membered rings are high yielding, and partial dehydrogenation of the adducts without aromatization is quite facile. However, aromatization of diquinone **11** to nonacene diquinone **7** is sluggish and low-yielding, and undecacene diquinone **12** could not be prepared from diquinone **15** under any of the conditions tried. On the basis of these model studies it appears that the number and size of the alkyl groups currently being employed are not adequate for solubilizing polyacene-polyquinone polymer **3**.

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References and Notes

1. Kivelson, S.; **Chapman, O.L.** *Phys. Rev. B* **1983**, *28*, 7236-7243.
 2. We have previously reported the synthesis of a macrocyclic cyclophane via double Diels-Alder cycloaddition of 5 to 6 in refluxing dioxane: Cory, R. M.; McPhail, C. L.; Dikmans, A. J.; Vittal, J.J. *Tetrahedron Lett.* **1996**, *37*, 1983-1986. At room temperature the major product is a polymer which we have assigned as 4 based on the similarity of its spectral properties to those of ribbon 19.
 3. For related studies see Kintzel, O.; Münch, W.; **Schlüter, A.-D.**; Godt, A. *J. Org. Chem.* **1996**, *61*, 7304-7308.
 4. Cory, R. M.; McPhail, C. L.; Dikmans, A. J. *Tetrahedron Lett.* **1993**, *34*, 7533-7536.
 5. Nugent, W. A.; Calabrese, J.C. *J. Am. Chem. Soc.* **1984**, *106*, 6422-6424.
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Comments

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