

# Beyond the Cyanine Limit: Peierls Distortion and Symmetry Collapse in a Polymethine Dye

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**Abstract:** Theory predicts that cyanine dyes and related linear systems undergo symmetry collapse and bond localization at long chain lengths. Beyond this “cyanine limit”, the properties of these systems do not extrapolate from their shorter counterparts. To test this prediction, dipyrdocyanines have been synthesized and shown to undergo such symmetry collapse with chain lengths as short as 13.

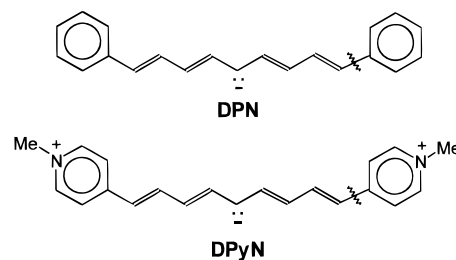
## Introduction

Optical band gap and bond alternation are two intimately related characteristics of linear polyenes which control a number of their properties, including optical polarizability and electrical conductivity. At one extreme lies polyacetylene. In the absence of bond alternation, the band gap would vanish and polyacetylene would be a true metal. However, a pseudo Jahn–Teller effect known as the Peierls distortion intervenes.<sup>1</sup> The resulting “dimerization” produces both the well-known bond alternation and the non-zero band gap. “Doping” of the polymer introduces charged defects (“solitons”) which ameliorate bond alternation within a finite domain.<sup>2</sup> At the other extreme lie cyanine dyes. As a result of the two dominant resonance forms with positive charge at opposite ends of a polymethine chain, each carbon–carbon bond is represented by a double bond in one form and a single in the other, leading to an average “bond and a half”, i.e., non-alternating, structure. Several crystal structures of cyanines of various types confirm the lack of bond alternation in cyanines.<sup>3</sup> In between are a host of intermediate forms, especially the merocyanines, for which bond alternation is a complex function of chain length, end groups, and solvent dielectric. Marder has pointed out a curious relationship between bond alternation and optical hyperpolarizability in linear polyenes<sup>4</sup> and has invoked Dähne’s notion of the “cyanine limit” as representing molecules with vanishing bond alternation.<sup>5</sup>

The absence of bond alternation in symmetrical cyanines presents a conundrum. On the one hand, within this simple prediction of the Dähne–Redaglia model,<sup>5</sup> the band gap for a cyanine of infinite length should vanish and the molecule should exhibit metallic behavior. On the other hand, such a molecule is within an end gap effect of polyacetylene, the prototypical (and insulating) bond-alternant molecule. A partial answer resolution to this conundrum is provided by early work of Tyutyulkov, who predicted that the limiting band gap of

polymethines should be non-zero and, rather, should depend on end gap effects.<sup>6</sup> More recently, using a free electron model, Kuhn determined that simple cyanines with 30 carbon atoms should exhibit asymmetric ground states.<sup>7</sup> Hush and co-workers have confirmed this prediction at a higher calculational level.<sup>8</sup> Together, these predictions relate the presence of bond alternation with the formation of a non-zero band gap. Thus, as a result of our continuing interest in the chemistry and physics of “molecular wires”, we embarked on an examination of this phenomenon by both calculation and experiment.

In order to maintain a systematic approach to the investigation of solitonic behavior in molecules, we investigated molecules isoelectronic with the subjects of our earlier studies, the diphenylpolyenyl anions **DPN**,<sup>9</sup> where DP represents diphenyl and N represents the number of chain atoms up to 17. In the present case, the *para* carbon of each phenyl was replaced by nitrogen, i.e., phenyl became 4-pyridinium (acronym **DPyN**).



For experimental studies, it was necessary to quaternize the terminal pyridines with a methyl group. The anions **DPN** were characterized by charge distribution placing the highest charge density at the center of the polyene chain. Although the cationic species **DPyN** are isoelectronic with the parent anionic **DPN**, we would expect that electrostatic interactions would cause the negative charge localized in the center of this moiety to migrate to one end or the other to annihilate one of the positive charges. Thus, each resulting structure corresponded to one of two

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(1) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. B* **1980**, *22*, 2099.

(2) (a) Tolbert, L. M.; Zhao, X. *Proceedings, NATO Workshop on Modular Chemistry*; Michl, J., Ed.; Kluwer Academic Publishers, in press. (b) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.

(3) (a) Potenza, J. A.; Zyontz, L.; Borowski, W. *Acta Crystallogr.* **1978**, *B34*, 193. (b) Kulpe, S.; Kuban, R.-J.; Schulz, B.; Dähne, S. *Cryst. Res. Technol.* **1987**, *22*. (c) Sieber, K.; Kutschabsky, L.; Kulpe, S. *Krist. Tech.* **1974**, *9*, 1111. (d) Zimer, V. B.; Kulpe, S. *J. Prakt. Chem.* **1975**, *317*, 185.

(4) (a) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Gilmour, S.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524. (b) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 3007.

(5) Dähne, S.; Radeglia, R. *Tetrahedron* **1971**, *27*, 3673.

(6) Tyutyulkov, N.; Dietz, F.; Favian, J.; Melhorn, A.; Tadjer, A. *Theor. Chim. Acta* **1981**, *60*, 185.

(7) Kuhn, C. *Synth. Met.* **1991**, *43*, 3681.

(8) (a) Reimers, J. R.; Craw, J. S.; Wong, A.; Bacsikay, G. B.; Hush, N. S. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1993**, *234*, 51. (b) Reimers, J. R.; Craw, J. S.; Hush, N. S. *Proceedings, U. S. Engineering Foundation Conference on Molecular Electronics: Science and Technology*, St. Thomas, U.S. V.I., 1991. (c) Craw, J. S.; Reimers, J. R.; Bacsikay, G. B.; Wong, A. T.; Hush, N. S. *Chem. Phys.* **1993**, *176*, 407–20.

(9) (a) Tolbert, L. M.; Ogle, M. E. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 279. (b) Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9519. (c) Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 5958.

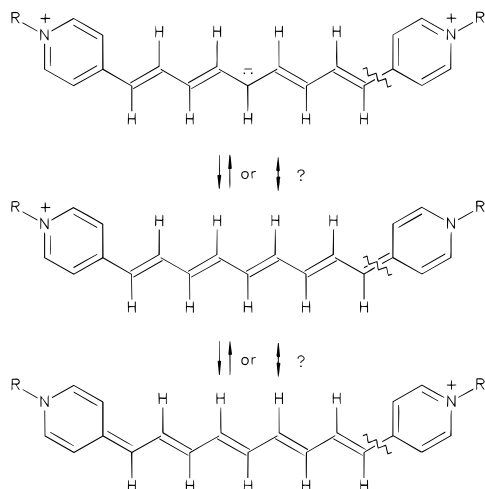


Figure 1. Charge migration in dipyriddyocyanines **DPyN**.

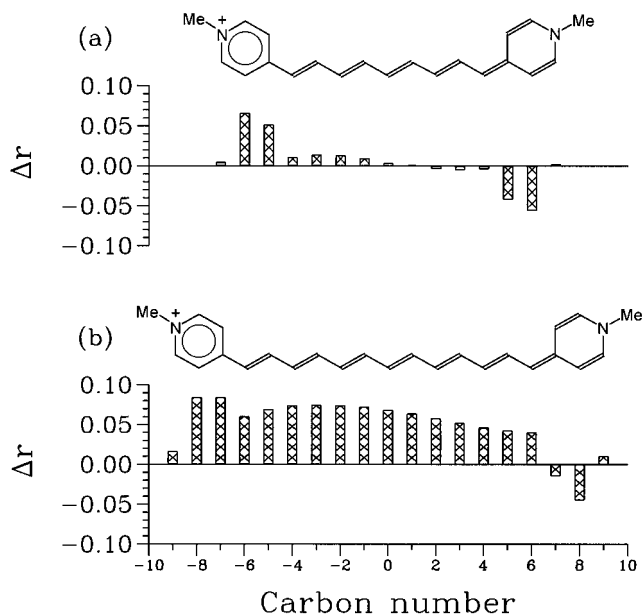


Figure 2. Bond alternation in (a) **DPy9** (b) **DPy13**.

equivalent resonance forms of a cyanine dye (see Figure 1). Again, at sufficient length the finite soliton width required that the two forms no longer be equivalent due to bond alternation induced by Peierls distortion. The electron density should localize at one end or the other of the polyene, but the ends could not communicate except through a solitonic (time-dependent) motion.

## Results

**Calculations.** Preliminary calculations at the AM1 level on cyanines constrained to planarity predict the formation of an asymmetric ground state as early as 13 carbon centers.<sup>10</sup> This phenomenon is visualized most readily by an examination of the bond alternation as a function of chain length. The dipyriddylnonatetraenyl cation (**DPy9**) has a symmetric ground state, with minimal bond alternation in the vicinity of the chain center (see Figure 2a, in which the difference in adjacent bond lengths,  $\Delta r$ , was plotted versus the position of the atom). In contrast, for the dipyriddyltridecahexaenyl cation (**DPy13**),  $C_{2v}$  symmetry is unstable relative to a Peierls distortion. A lifting of the symmetry to produce the asymmetric ground state is shown in Figure 2b. Thus, **DPy9** clearly exhibits  $C_{2v}$  symmetry

(10) Tolbert, L. M.; Zhao, X. *Synth. Met.* **1993**, 55–57, 4788.

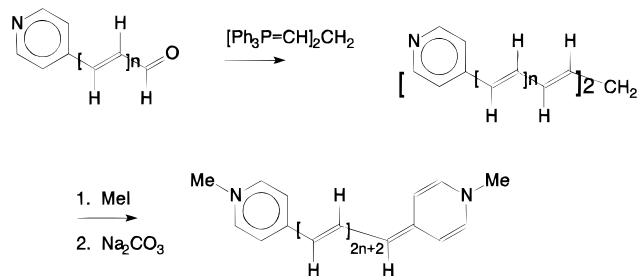


Figure 3. Synthesis of cyanines **DPyN**,  $N = 5, 9, 13$ .

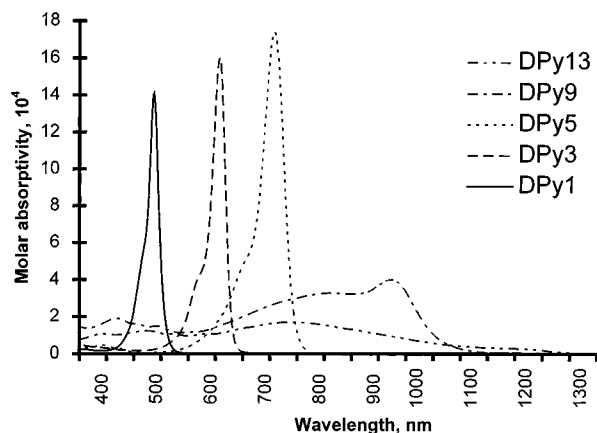


Figure 4. Spectra of **DPyN** cations in  $\text{Me}_2\text{SO}$ .

corresponding to the classical resonance picture of cyanines, while **DPy13** does not.

**Synthesis and Spectroscopy of Cyanines.** In order to confirm this phenomenon, we synthesized cyanines of type **DPyN**, specifically, **DPy1**, **DPy3**, **DPy5**, **DPy9**, and **DPy13**. Syntheses of **DPy1** and **DPy3** were accomplished following literature procedures. The remaining molecules were synthesized following a modification of our procedures for the diphenylpolyenyl anions using conventional Wittig methodology<sup>11</sup> (see Figure 3). The cyanines were generated by deprotonation of the intermediate bis(pyridinium)polyenes, producing colors ranging from deep red to green to blue. Cyanine **DPy13** gave several early indications of uniqueness, including extreme oxygen sensitivity, requiring inert atmosphere handling, and incomplete deprotonation, or, for strong bases, decomposition. Optimum conditions for generating **DPy13** involved use of quinuclidine base in  $\text{Me}_2\text{SO}$ , which nevertheless gave incomplete deprotonation. The absorption spectra of the dipyriddyocyanines following deprotonation are shown in Figure 4. Particularly noteworthy is the absorption spectrum of **DPy13**, which is broad and featureless, in contrast to the shorter members of the series. At higher concentrations, the shape of the absorption of **DPy13** at ca.  $13\,500\text{ cm}^{-1}$  emerges and shows a remarkable solvent dependence to both maximum and peak width (see Figure 5). Finally, the infrared absorption spectrum of **DPy13** exhibits a new absorption at  $1729\text{ cm}^{-1}$  which is absent in the earlier members of the series (see Figure 6).

Recently, following the efforts of Brédas, Silbey, and others,<sup>12</sup> based on the early work of Kuhn,<sup>13</sup> we have adopted an approach based on the particle in a box model, which originates from modified free electron theory. This model predicts that the absorption behavior of one-dimensional conjugated systems can be described by eq 1:

(11) Wittig, G.; Eggers, H.; Duffner, P. *Annalen* **1958**, 619, 10.

(12) Brédas, J.-L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, 105, 6555.

(13) (a) Kuhn, H. *Helv. Chim. Acta* **1948**, 31, 1441. (b) Kuhn, H. *Helv. Chim. Acta* **1949**, 32, 2247.

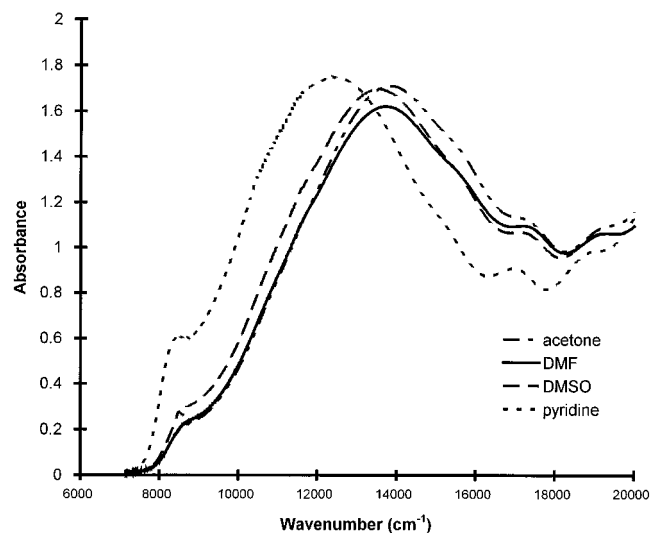


Figure 5. Absorption spectrum of **DPy13** in different solvents.

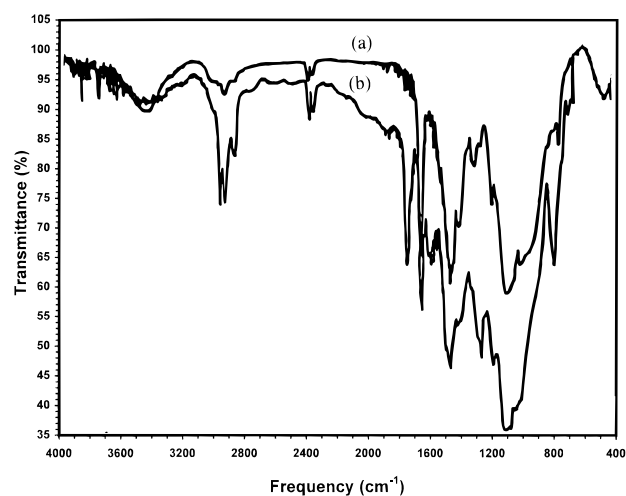


Figure 6. Infrared absorption spectra of (a) **DPy9** and (b) **DPy13**.

$$\Delta E = hc/\lambda = E_{\infty} + k/(N_{\pi} + C) = E_{\infty} + k/N_{\text{eff}} \quad (1)$$

In eq 1,  $N_{\pi}$  is the number of  $\pi$ -electrons involved in the conjugation,  $C$  is a function of the terminal groups; the combination of  $N_{\pi} + C$  corresponds to effective conjugation length,  $N_{\text{eff}}$ . The intercept  $E_{\infty}$  corresponds to the band gap at infinite chain length. For **DPyN** or **DPN**, use of the more convenient absorption maximum energies and  $C = 4$  per phenyl or pyridine provided a linear relationship, with a limiting solitonic intercept of ca. 0.6 eV for dyes **DPN** ( $N = 1-13$ ) and a zero intercept for dyes **DPy1** through **DPy9**. In contrast, **DPy13** exhibits a remarkable hypsochromic shift relative to **DPy9** (see Figure 7).

## Discussion

The spectral properties, as well as anecdotal chemical stability, of **DPy13** are clearly in accord with a profound shift in electronic structure for this species, which we interpret to be the result of symmetry collapse. This evidence includes the apparent onset of an optical electron transfer band, the solvatochromicity, and the onset of a new infrared absorption band consistent with a polarized C=N band.

**Optical Electron Transfer in the DPy13 Absorption Spectrum.** The structureless shape of the broad absorption band in **DPy13** (Figure 5) differs radically from the sharp peak absorptions of the cyanine dyes, although **DPy9** appears to exhibit a broadening of the strongly allowed  $\pi$ - $\pi$  absorption.

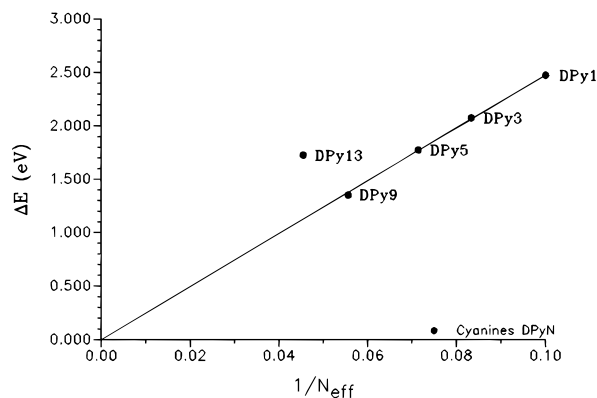


Figure 7. Energy gap  $\Delta E$  vs  $(N_{\text{eff}})^{-1}$  for cyanines **DPyN**.

Similar phenomena in other cyanine systems were first reported by Brooker et al. in their studies of thiocyanine series.<sup>14</sup> They attributed these behaviors to *cis-trans* isomerism, in which *cis* isomers, presumably, have shorter effective chromophoric chain lengths. However, the coupling constants evident in the <sup>1</sup>H-NMR spectrum of **DPy13** are in the same 12–14 Hz range characteristic of the other cyanines and are consistent with the *all-trans* configuration (see Experimental Section).

Another possible explanation of these observations involves dye aggregation. While it is generally accepted that cyanines do not aggregate in organic solvents, these dyes are known to form aggregates in aqueous solution.<sup>14</sup> It was observed that, for many cyanines in aqueous solutions, the bands of longest wavelength absorptions in dilute solution become weaker as the concentration is increased and new absorption bands appear. To exclude the possibility of dye aggregation for **DPy13**, concentration dependence studies were conducted in organic solvents. Solutions of **DPy13** followed Beer's law at least in the range below  $10^{-4}$  M. The absorption features, including the relative intensity of the peaks and the positions and the shapes of the absorption bands, did not change with concentration. No new absorption bands were observed as the concentration increased. The proton chemical shifts of this molecule also showed no concentration-dependent changes associated with significant aggregation of **DPy13**.<sup>15</sup> Thus, no significant dye aggregation of **DPy13** was in evidence in organic solvents.<sup>16</sup> If the broad absorption in **DPy13** is not attributable to aggregation, what can account for this appearance? These absorptions are most reminiscent of those associated with intervalence electron transfer absorption in weakly coupled binuclear transition metal complexes. A common feature of these absorptions is their large band half-width, typically<sup>17</sup> around  $5000 \text{ cm}^{-1}$ . One might ask if the broad absorption in the spectrum of **DPy13** reflects an analogous optical electron transfer. The theory for these transitions has been developed extensively by Hush.<sup>18</sup> Using this approach, and for the temperature limit defined by  $h\nu \ll kT$  and  $T = 300 \text{ K}$ , a simple relationship has been developed for intervalence charge transfer absorptions:<sup>19</sup>

$$\Delta = (2310\nu_{\text{IT}})^{1/2} \quad (2)$$

(14) Brooker, L. G. S. In *Theory of the Photographic Process*, 3rd ed.; Hillson, P. J., Sutherns, E. A., Eds., Macmillan: New York, 1991; p 204.

(15) Graves, R. E.; Rose, P. I. *J. Phys. Chem.* **1975**, *79*, 746.

(16) Aggregation was evident for some of the shorter cyanines in water. This aggregation could be defeated by addition of cyclodextrins.

(17) Day, P. *NATO, ASI Ser., Series C.* **1975**, *20*, 1.

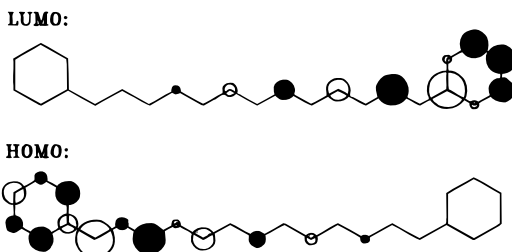
(18) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Prog. Inorg. Chem.* **1982**, *30*, 210. (c) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 12.

(19) Ludi, A. *Chimia* **1972**, *26*, 647. Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1964.

**Table 1.** Observed and Calculated Band Half-Widths for **DPy13**

solvent	$\nu_{IT}^a$	$\Delta_{calcd}^b$	$\Delta_{obsd}^c$
acetone	13 800	5650	5840
Me <sub>2</sub> SO	13 500	5600	5720
DMF	13 700	5630	5840
pyridine	12 300	5330	5300

<sup>a</sup> Optical transition energies are in cm<sup>-1</sup>. <sup>b</sup>  $\Delta_{calcd}$  is the calculated band half-width in cm<sup>-1</sup> from eq 2. <sup>c</sup>  $\Delta_{obsd}$  is the observed ( $\pm 20\%$ ) band half-width in cm<sup>-1</sup>.

**Figure 8.** Representations of lowest unoccupied and highest occupied molecular orbitals of **DPy13**.

For Equation 2,  $\nu_{IT}$  is the energy, in cm<sup>-1</sup>, of the intervalence absorption band and  $\Delta$  is the absorption half-width. One might ask if this relationship holds for optical electron transfer bands associated with symmetry-collapsed cyanines. The long-wavelength absorption of **DPy13** has the typical intervalence band half-width, ca. 5000–6000 cm<sup>-1</sup>. In Table 1 are shown the calculated band half-widths  $\Delta$  from eq 2 and the observed band half-widths in different solvents from Figure 5 obtained by triangulation of the low-frequency half-band. The agreement, ca. 15%, between  $\Delta_{obsd}$  and  $\Delta_{calcd}$  suggests that the Hush model for intervalence transfer in binuclear complexes is a satisfactory description of the absorptive behaviors of **DPy13** and verifies the charge transfer character of this absorption band.

The charge transfer character of the first excitation band of **DPy13** can be readily understood by an examination of the AM1 coefficients of the ground and first excited state molecular orbitals of the molecule (see Figure 8). While the positive charge is localized at one end in the ground state, it clearly migrates to the other end in the first excited state. These results suggest that **DPy13** is a Robin–Day class II system with a double minimum potential surface and a degenerate ground state,<sup>20</sup> i.e., a Peierls distorted molecule.

**Solvatochromicity.** While the visible absorption spectra of symmetrical cyanines exhibit very limited solvatochromism,<sup>21</sup> consistent with symmetrical ground and excited states, if the longest wavelength absorption band of **DPy13** is analogous to the intervalence charge transfer (IT) for binuclear transition metal complexes, a large solvatochromic shift should be observed. With the assumption of a dielectric continuum model, the Hush approach has been used to analyze the dependence of transition energy  $E_{IT}$  on solvent polarization (eq 3).<sup>22</sup>

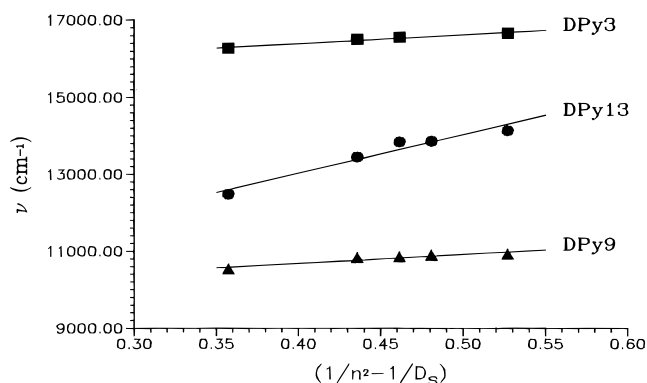
$$E_{IT} = h\nu_{IT} = \chi_i + e^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left( \frac{1}{n^2} - \frac{1}{D} \right) \quad (3)$$

Here  $(1/n^2 - 1/D)$  is the solvent polarity defined in terms of index of refraction  $n$  and solvent dielectric  $D$ ,  $\chi_i$  is the gas phase absorption energy, and  $e^2(1/(2a_1) + 1/(2a_2) - 1/d)$  describes the absorption dipole geometry.<sup>22</sup> When the absorptions shown

(20) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(21) West, W.; Geddes, A. L. *J. Phys. Chem.* **1964**, *68*, 837.

(22) For a discussion, see: (a) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731. (b) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827.

**Figure 9.** Solvatochromic behavior for **DPy3**, **DPy9**, and **DPy13**.

in Figure 5 are plotted vs  $(1/n^2 - 1/D)$  (see Figure 9), the slope obtained is comparable to that of the merocyanines, which clearly suggests that the electronic structure of **DPy13** is closer to that of merocyanines rather than that of classical cyanines. Finally, the additional infrared band exhibited by **DPy13** at 1739 cm<sup>-1</sup> suggests the onset of double-bond polarization to form the  $-\text{HC}=\text{CHCH}=\text{N}^+\text{R}$  moiety absent from the symmetrical **DPy9** (see Figure 6). Thus, this observation is also in accord with a bond-alternating structure and suggests that the onset of the Peierls distortion may occur at a shorter chain length than previously anticipated.

## Conclusions

The concept of resonance has been fundamental to our understanding of reactivity in conjugated systems. Our work with polyenyl anions has demonstrated, however, that a non-bonding electron pair in an unsaturated system is confined within a ca. 30 carbon atom framework, corresponding to the soliton width. The fact that a cyanine such as **DPy13** should exhibit the onset of bond alternation at a chain length of 13 carbon atoms would seem to shorten that confinement width. This contradiction vanishes when one realizes that **DPy13** has the largest HOMO coefficient at the formal trivalent nitrogen. In this case, delocalization can occur over only one-half the region occurring when the highest electron density is in the center of the chain. Beyond the “cyanine limit,” i.e., for bond-localized cyanines for which optical electron transfer is weak, the optical excitations reduce to the local ones predicted by Tyutyulkov.<sup>6</sup> Thus, the delocalization width of 30 re-emerges as a fundamental limit to delocalization in a polyene system. This fact alone means that the possibility of achieving metallic, i.e., zero band gap, behavior vanishes, leaving solitonic or polaronic *time-dependent* processes available for long-range molecular level conduction. In this context, it is important to realize that the limiting rate for such processes is quite slow, i.e., approximately three times the speed of sound.<sup>23</sup>

## Experimental Section

**Materials.** For air-sensitive materials, acetone and acetonitrile were distilled over CaH<sub>2</sub>, then subjected to deoxygenation by several freeze–pump–thaw cycles with argon purging, and stored under argon. For vacuum line manipulations, argon (HoloX, Atlanta, Ga) was dried by passing through a series of columns containing Drierite and P<sub>2</sub>O<sub>5</sub>. For inert atmosphere applications, argon was deoxygenated with a BASF catalyst (R-311) drying train. Diethyl ether and tetrahydrofuran were distilled under argon immediately before use from potassium/sodium alloy containing benzophenone ketyl. Dimethyl sulfoxide (Me<sub>2</sub>SO, Fisher) was purified according to the procedure of Bordwell.<sup>24</sup> Me<sub>2</sub>

(23) Kuhn, C.; van Gunsteren, W. F.; *Solid State Commun.* **1993**, *87*, 203. (b) Kuhn, C. *Synth. Met.* **1993**, *57*, 4350.

(24) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucher, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

SO- $d_6$  (Aldrich, 99.9% isotopic purity) was dried and deoxygenated in the same fashion. Pyridine (Fisher, reagent) was deoxygenated by several freeze-pump-thaw cycles under an argon atmosphere. The deoxygenated pyridine was stored under argon in a glovebox.

Diisopropylamine (Aldrich, 99+%) was dried over CaH<sub>2</sub> for at least 1 day and distilled over CaH<sub>2</sub> immediately before use. *cis*-1-Methoxy-1-buten-3-yne (Aldrich), received as a 50% w/w solution in methanol/water (4:1), was purified according to the method of Krause and Frazier.<sup>25</sup> Piperidine (Aldrich, 99%) was distilled over molecular sieves before use.

Morpholine acetate was afforded by a reaction of 1 equiv of morpholine (Aldrich, 99%) and 1 equiv of acetate acid in ethanol. The exothermic reaction yielded a large amount of white precipitate in 10 min at room temperature. Recrystallizations from methanol yielded the pure compound as colorless crystals (mp 106–109 °C). Trimethylenebis(triphenylphosphonium) bromide was synthesized according to a literature method<sup>26</sup> and had mp 335–336 °C (lit.<sup>32</sup> 335–336 °C).

**Manipulations.** All glassware, including cannulas and syringes, was dried at 135 °C for at least 24 h prior to use. Glassware was allowed to cool under a flow of argon. Syringes and cannulas were flushed with argon immediately before sample introduction. For anaerobic reaction conditions, transfer of samples was conducted via stainless steel cannulas or syringes. Inert conditions were maintained by an atmosphere of argon.

Due to the extreme sensitivity of long-chain cyanines to oxygen, a number of operations were conducted in a Vacuum Atmospheres glovebox, containing an atmosphere of argon. The atmosphere inside the glovebox was constantly deoxygenated with a dry train containing a BASF catalyst (R-311). The dry train was maintained by routine regeneration every 2 months. The glovebox was flushed with argon (10–12 times of the volume of the dry box) prior to use if it had not been used for a long period of time or large quantity of solvents were used.

**Instrumentation.** Infrared (IR) spectra in the region of 2.5–25  $\mu\text{m}$  (4000–400  $\text{cm}^{-1}$ ) were recorded on a Nicolet 520 FTIR equipment. Solid samples were recorded in the potassium bromide (KBr) pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 300 spectrometer in Me<sub>2</sub>SO- $d_6$  (<sup>1</sup>H, 2.49 ppm; <sup>13</sup>C, 39.5 ppm), CDCl<sub>3</sub> (<sup>1</sup>H, 7.24 ppm) or acetone- $d_6$  (<sup>1</sup>H, 2.04 ppm). Chemical shifts were reported in ppm with the solvent peaks as references.

For the air-sensitive samples, a special NMR tube connected with a J. Young greaseless valve (Aldrich) was used. The valve consisted of a borosilicate glass valve body and an O-ring-sealed PTFE piston with an axial bore. A simple glass tube was used to connect the tube to a vacuum apparatus.

UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer, which has a scan range of 190–2500 nm. Spectra for air-sensitive compounds were taken with a specially constructed, calibrated spectrophotometric cell.<sup>27</sup>

Mass spectra (MS) were recorded using a VG analytical 70-SE spectrometer and are reported with mass-to-charge ratio and the intensity indicated. High-resolution mass spectra were used to determine the identity of the compounds.

**Computer Calculations.** Linear least-squares statistics were performed using Excel 3.0 on a IBM 486 PC. Semiempirical (AM1) calculations were performed on a Silicon Graphics Indigo workstation using Spartan 3.0 from Wavefunction, Inc.

***N,N*-Dimethyl-4,4'-dipyridocyanine iodide (DPy1).** DPy1 was synthesized by a modified procedure of Sprague and Brooker.<sup>28,29</sup> Benzenethiol (Aldrich, 4.70 g, 0.430 mol) was cooled to 0 °C, and chloropyridine (3.34 g, 0.300 mol), obtained by neutralization of the

hydrochloride with aqueous ammonia, was added. The mixture was heated at 100 °C for 10 min, neutralized with aqueous ammonia, and extracted with ether (3 × 50 mL). The combined organic layers were concentrated and distilled *in vacuo* (bp 128–130 °C/2 mmHg) to yield 4-(phenylthio)pyridine as a colorless oil. The oil was treated with 2 equiv of MeI and heated to gentle reflux for 30 min. The resulting solid was recrystallized (MeOH) to yield 7.12 g (75%) of *N*-methyl-4-(phenylthio)pyridinium iodide as light yellow crystals (mp 172–174 °C, lit.<sup>34</sup> 174–176 °C). <sup>1</sup>H NMR (Me<sub>2</sub>SO):  $\delta$  8.61 (2H, d,  $J$  = 6.9 Hz), 7.71–7.65 (5H, m), 7.58 (2H, d,  $J$  = 7.2 Hz), 4.15 (3H, s).

A mixture of *N*-methyl-4-picolinium toluenesulfonate (2.91 g, 10.0 mol), *N*-methyl-4-(phenylthio)pyridinium iodide (3.43 g, 10.0 mol), triethylamine (3.30 g, 30.0 mol), and 1-propanol (99+%, Aldrich, 16 mL) was heated at reflux for 90 min. After cooling, the mixture was added to ether (200 mL), and the resulting precipitate recrystallized from ethanol to afford *N,N,N*-trimethyl-4,4',4''-tripyrindocyanine as a dark red solid mp 284–286 °C (dec). The concentrated mother liquor was chromatographed on alumina (9:1 acetone/methanol) to yield a red solid. Recrystallization from methanol afforded 0.170 g of red crystals (0.520 mmol, 5%), mp 187–189 °C, lit.<sup>30</sup> 174–176 °C). <sup>1</sup>H NMR (Me<sub>2</sub>SO):  $\delta$  7.72 (4H, d,  $J$  = 6.9 Hz), 7.03 (4H, broad), 5.42 (1H, s), 3.71 (6H, s). MS ( $m/z$ , intensity):<sup>31</sup> 320 (8), 199 (100, M<sup>+</sup>), 184 (7, M – CH<sub>3</sub><sup>+</sup>). FAB/HRMS: calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>I 199.1235; found 199.1252. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1634.7, 1557.6, 1542.1, 1522.0, 1188.2. UV-vis (Me<sub>2</sub>SO): 486.0 nm ( $1.41 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ), lit.<sup>35</sup> 483 nm ( $1.26 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , in ethanol).

***N,N*-Dimethyl-4,4'-dipyridocarbocyanine Iodide (DPy3).**<sup>32</sup> A mixture of *N*-methyl-4-picoline iodide (4.7 g, 20 mmol) and diethoxymethyl acetate (99%, 1.6 g, 10 mmol) in 10 mL of piperidine was heated to 120 °C for 3 h. The resulting blue precipitate was collected and washed with ether. Alumina column chromatography (10:90 CH<sub>3</sub>OH/acetone) and recrystallization from absolute ethanol afforded small blue crystals (0.50 g, 14%, mp 209–210 °C (dec.)). <sup>1</sup>H NMR (Me<sub>2</sub>SO):  $\delta$  8.07 (1H, t,  $J$  = 13.4 Hz), 7.70 (4H, d,  $J$  = 7.15 Hz), 7.10 (4H,  $J$  = 7.20 Hz, broad peak at room temperature, doublet at 120 °C), 5.68 (2H, d,  $J$  = 13.4 Hz), 3.70 (6H, s). MS ( $m/z$ ):<sup>35</sup> 346 (adduct), 225 (M<sup>+</sup>), 210 (M – CH<sub>3</sub><sup>+</sup>). IR (KBr pellet,  $\text{cm}^{-1}$ ): 1637.1, 1558.4, 1530.8, 1485.3, 1465.8, 1419.0, 1290.9, 1143.5, 1010.7, 959.8. UV-vis (Me<sub>2</sub>SO): 606 nm ( $1.60 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ).

***N,N*-Dimethyl-4,4'-dipyridodicarbocyanine Iodide (DPy5).** 1,5-Dipyridyl-1,3-pentadiene was prepared by a modification of the procedure of Wittig et al.<sup>11</sup> A solution of 1,3-propanediylidenebis(triphenylphosphorane) prepared from 4.54 g (6.25 mmol) of trimethylenebis(triphenylphosphonium) dibromide and 12.5 mmol of lithium diisopropylamide in tetrahydrofuran was treated at –78 °C with pyridinecarboxaldehyde (1.34 g, 12.5 mmol) in tetrahydrofuran (10 mL). The mixture was kept at –78 °C for 3 h and quenched by addition of 1 mL of concentrated HCl in 5 mL of methanol. After evaporation of solvent, sodium bicarbonate (1.3 g in 50 mL H<sub>2</sub>O) was added to adjust to pH 8. The mixture was extracted with chloroform (3 × 50 mL). The organic extracts were combined, dried, and concentrated. The resultant red solid was subjected to silica gel column chromatography (2% methanol/chloroform). 1,5-Dipyridyl-1,4-pentadiene was obtained as a red oil (0.67 g, 49%) and was stored under an argon atmosphere at –30 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.56–8.50 (4H, m), 7.25–7.20 (2H, m), 7.18–7.04 (2H, m), 6.96 (1H, dd,  $J$  = 10.5 Hz, 15.6 Hz), 6.43 (1H, d,  $J$  = 15.9 Hz), 6.30 (1H, dd,  $J$  = 10.5 Hz, 14.4 Hz), 6.05 (1H, dt,  $J$  = 7.1 Hz, 14.6 Hz), 3.51 (2H, d,  $J$  = 7.2 Hz).

A sample of 1,5-dipyridyl-1,3-pentadiene (48 mg, 0.22 mmol) was dissolved in acetone (5 mL) and treated with methyl iodide (1.0 mL, 16 mmol). After 18 h at room temperature, the supernatant was decanted, the red precipitate was dissolved in methanol, and the solution was poured into ether. The resulting precipitate was filtered and washed with ether to afford pentadienyl-1,5-bis(methyl-4-pyridinium) diiodide as a yellow powder (80 mg, 73%). <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  8.51 (2H, d,  $J$  = 6.6 Hz), 8.38 (2H, d,  $J$  = 6.7 Hz), 7.75–7.78 (4H, m), 7.33 (1H,

(25) Kraus, G. A.; Frazier, K. *Tetrahedron Lett.* **1978**, 3195.

(26) Homer, L.; Hoffman, H.; Klink, W.; Ertel, E.; Toscano, V. G. *Chem. Ber.* **1962**, 95, 581.

(27) Zhao, Xiaodong, Ph. D. Thesis, Georgia Institute of Technology, Atlanta, GA 1995.

(28) Sprague, R. H.; Brooker, L. G. S. *J. Am. Chem. Soc.* **1937**, 59, 2697.

(29) Leubner, I. H. *J. Org. Chem.* **1973**, 38, 1098.

(30) Leubner, I. H. *Nucl. Magn. Reson.* **1974**, 6, 253.

(31) Lemire, S. W.; Zhao, X.; Tolbert, L. M.; Busch, K. L. *J. Am. Soc. Mass Spectrom.* **1994**, 5, 1017.

(32) Dent, S. G.; Brooker, L. G. S. U.S. Pat. 2,537,880 (Jan 9, 1951).

(33) Leitis, L.; Rubina, K.; Goldberg, Yu. Sh.; Jansone, D.; Shimanskaya, M. V. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1980**, 4, 469.

(34) Hagedorn, H.; Hohler, W. *Angew. Chem., Int. Ed. Engl.* **1975**, 14, 486.

(35) Wollenberg, R. H. *Tetrahedron Lett.* **1978**, 717.

dd,  $J = 10.3$  Hz, 15.6 Hz), 6.59 (1H, d,  $J = 15.5$  Hz), 6.43 (1H, dd,  $J = 15.4$  Hz, 10.4 Hz), 6.28 (1H, m), 4.63 (3H, s), 4.18 (3H, s), 3.73 (2H, d,  $J = 6.6$  Hz).

Pentadienyl-1,5-bis(methyl-4-pyridinium) diiodide (120 mg, 0.24 mmol) was dissolved in 3 mL of 2:1 Me<sub>2</sub>SO/CH<sub>2</sub>Cl<sub>2</sub>. Piperidine (0.5 mL, 5.1 mmol) was added, and the solution was stirred at room temperature for 2 min and poured into ether (150 mL). The dark blue precipitate was collected and subjected to alumina column chromatography (15% methanol/acetone). Recrystallization from ethanol of the first blue band produced a green solid (42 mg, 47%, mp > 320 °C). <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>): δ 7.71 (4H, d,  $J = 7.1$  Hz), 7.52 (2H, t,  $J = 13.0$  Hz), 6.98 (4H, d,  $J = 6.5$  Hz), 5.98 (1H, t,  $J = 12.1$  Hz), 5.75 (2H, d,  $J = 13.3$  Hz), 3.71 (6H, s). IR (KBr pellet, cm<sup>-1</sup>): 1545.5, 1545.7, 1505.8, 1482.4, 1414.6, 1111.1, 1017.4. MS (*m/z*):<sup>35</sup> 372 (adduct), 251 (M<sup>+</sup>), 236 (M - CH<sub>3</sub><sup>+</sup>). UV-vis (Me<sub>2</sub>SO): 707 nm ( $1.74 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>).

***N,N*-Dimethyl-4,4'-dipyridotetracarboyanine Iodide (DPy9).** 3-(4-Pyridyl)-2-propenal was prepared from 4-pyridinecarboxaldehyde (1.6 g, 0.015 mol), acetaldehyde (0.66 g, 0.015 mol), and morpholine acetate (0.22 g, 1.5 mmol). Silica gel column chromatography (ethyl acetate) afforded 3-(4-pyridyl)-prop-2-enal as a light yellow solid. Sublimation (70 °C/0.5 Torr) yielded 1.48 g (74%) of light yellow crystals (mp 36–38 °C, lit. 35–36 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.79 (1H, d,  $J = 7.5$  Hz), 8.73 (2H, d,  $J = 6.0$  Hz), 7.45 (1H, d,  $J = 15.6$  Hz), 7.43 (2H, d); 6.85 (1H, dd,  $J = 7.5$  Hz, 16.2 Hz). MS (*m/z*, intensity): 133.1 (17.2), 104.0 (14.0), 58.0 (22.7), 43.0 (100.0). FAB/HRMS: calcd for C<sub>8</sub>H<sub>7</sub>NO 133.05276; found 133.05278.

A 50 mL tetrahydrofuran solution of 1,3-propanediylidenebis(triphenylphosphorane) produced from 15 mmol of lithium diisopropylamide and 5.5 g (7.5 mmol) of trimethylenebis(triphenylphosphonium) dibromide (5.5 g, 7.5 mmol) was added to a solution of 3-(4-pyridyl)-2-propenal (2.0 g, 15 mmol) in 50 mL of tetrahydrofuran (ca. 50 mL) at -78 °C. After 1 h at -78 °C for 1 h and 2 h at -50 °C, the mixture was quenched with 1 mL of acetic acid in 5 mL of water. The volume was reduced under reduced pressure, and the resultant aqueous solution was neutralized with aqueous ammonia and extracted with chloroform (3 × 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated to afford a red tar. Silica gel chromatography (2% methanol/chloroform) afforded 1,9-dipyridylnona-1,3,6,8-tetraene as a light red oil (0.60 g, 29%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.52 (4H, d,  $J = 5.8$  Hz), 7.35 (2H, dd), 7.28 (4H, d), 6.52 (2H, d,  $J = 15.4$  Hz), 6.26 (2H, t,  $J = 10.8$  Hz), 5.70 (2H, m), 3.33 (2H, t,  $J = 8.0$  Hz).

A sample of 1,5-dipyridylnona-1,3,6,8-tetraene (50 mg, 0.18 mmol) was dissolved in acetone (3 mL) and treated with methyl iodide (1.0 mL, 16 mmol). After 18 h at room temperature, the supernatant solution was decanted and the red precipitate was dissolved in Me<sub>2</sub>SO/methylene chloride (3:1). The solution was poured into ether, and nona-1,3,6,8-tetraenyl-1,5-bis(*N*-methyl-4-pyridinium) diiodide (DPy9-H) precipitated as a yellow solid and was collected by filtration (62 mg, 62%, mp 127–135 °C (dec.)). <sup>1</sup>H NMR (Me<sub>2</sub>SO): δ 8.88 (2H, d,  $J = 6.0$  Hz), 8.76 (2H, d,  $J = 6.6$  Hz), 8.08 (2H, d,  $J = 6.9$  Hz), 7.98 (2H, d,  $J = 6.3$  Hz), 7.71 (1H, dd,  $J = 10.5$  Hz, 15.6 Hz), 6.83–6.75 (2H, m), 6.67–6.34 (4H, m), 6.08 (1H, m), 4.29 (3H, s), 4.20 (3H, s), 3.79 (2H, d,  $J = 7.2$  Hz).

The following procedure was conducted in a drybox: Nona-1,3,6,8-tetraenyl-1,9-bis(*N*-methyl-4-pyridinium) diiodide (72 mg, 0.13 mmol) was dissolved in Me<sub>2</sub>SO/methylene chloride (2:1, 2 mL). Piperidine (0.30 mL, 3.1 mmol) in Me<sub>2</sub>SO (2 mL) was added. The green-blue solution was stirred for 2 min and poured into ether under vigorous stirring. The dark blue precipitate was filtered and subjected to alumina column chromatography (15:85 methanol/acetone). The green band was extracted with acetone to yield approximately 30 mg of *N,N*-dimethyl-4,4'-dipyridotetracarboyanine iodide (DPy9) as a dark green solid. <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>): 7.70 (4H, d,  $J = 7.3$  Hz), 7.32 (1H, t,  $J = 13.1$  Hz), 7.03 (4H, d,  $J = 7.4$  Hz), 6.76 (2H, t,  $J = 12.7$  Hz), 6.19–6.05 (4H, m), 5.85 (2H, d,  $J = 13.9$  Hz), 3.70 (6H, s). IR (KBr pellet, cm<sup>-1</sup>): 1636.4, 1456.7, 1404.8, 1101.2, 1011.4. UV-vis (Me<sub>2</sub>SO): 920 nm (ca.  $4.0 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>).

**5-(4-Pyridyl)-penta-2,4-dienal.** To a solution of 1-tri-*n*-butylstannyl-4-methoxybuta-1,3-diene<sup>35</sup> (10.4 g, 27.9 mmol) in tetrahydrofuran (100 mL) was added butyllithium (12.2 mL of 2.5 M in hexanes) at

-78 °C under argon. After 30 min, pyridinecarboxaldehyde (2.98 g, 27.9 mmol) was added. The mixture was stirred at -78 °C for 3 h and quenched with sodium bicarbonate/water/tetrahydrofuran (2.0 g/10 mL/10 mL). The solvent was removed, and the mixture was extracted with ether (3 × 100 mL). The ether extracts were combined and concentrated to yield a clear liquid containing a red gum. The clear liquid (tetrabutyltin) was decanted, and the red gum was dissolved in 1:1 tetrahydrofuran/water. The pH was adjusted to 2 with 1 M aqueous HCl. The solution was stirred at room temperature for 3 h, and the pH was adjusted to 8.5 with aqueous ammonia. After reduction of the volume under reduced pressure, the mixture was extracted with ether (3 × 100 mL), and the combined organic fractions were concentrated under reduced pressure. The yellow solid was subjected to chromatography on silica gel (ethyl acetate). 5-(4-Pyridyl)-penta-2,4-dienal was obtained as a light yellow solid (2.53 g, 57%, mp 55–57 °C). The aldehyde was also prepared by oxidation of 5-(4-pyridyl)-2,4-pentadienol.<sup>26</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.68 (2H, d,  $J = 7.8$  Hz), 8.64 (2H, m), 7.35 (2H, m), 7.34–7.12 (2H, m), 6.95 (1H, d,  $J = 14.9$  Hz), 6.38 (1H, dd,  $J = 8.0$  Hz; 15.2 Hz). IR (KBr pellet, cm<sup>-1</sup>): 1683.4, 1669.6, 1602.4, 1156.9, 1118.2, 995.7. MS (*m/z*, intensity): 159.1 (87.8, M<sup>+</sup>), 81.0 (50.8), 77.0 (40.3). FAB/HRMS: calcd for C<sub>10</sub>H<sub>9</sub>NO 159.0684; found 159.0684.

***N,N*-Dimethyl-4,4'-dipyridohexacarboyanine Iodide (DPy13).** A 200 mL tetrahydrofuran solution of 1,3-propanediylidenebis(triphenylphosphorane) prepared from trimethylenebis(triphenylphosphonium) bromide (5.00 g, 6.80 mmol) and 13.8 mmol *n*-butyllithium was added to a solution of 5-(4-pyridyl)-penta-2,4-dienal (1.31 g, 13.7 mmol) in 15 mL of tetrahydrofuran at -78 °C. After 3 h at -78 °C and 1 h at -50 °C, 1 mL of acetic acid and 5 mL of water were added. The volume of solvent was reduced evaporated under reduced pressure, and the pH of the solution was adjusted to >8 with aqueous ammonia. After extraction with CHCl<sub>3</sub> (3 × 50 mL), the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated to afford a red tar. Silica gel column chromatography (25:75 tetrahydrofuran/CH<sub>2</sub>Cl<sub>2</sub>) yielded 1,13-dipyridyltrideca-1,3,5,8,10,12-hexaene as a light red oil (0.40 g, 18%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.54 (4H, m), 7.26 (4H, m), 7.08–6.96 (2H, m), 6.73 (1H, dd,  $J = 15.2$  Hz, 9.8 Hz), 6.55–6.16 (7H, m), 5.86 (1H, m), 5.61 (1H, dd), 3.11 (2H, t,  $J = 7.8$  Hz).

1,13-Dipyridyltrideca-1,3,5,8,10,12-hexaene (115 mg, 0.350 mmol) dissolved in 5 mL of acetone was treated with methyl iodide (1.0 mL, 16 mmol). After 18 h at room temperature, the supernatant solution was decanted and the remaining red precipitate was dissolved in Me<sub>2</sub>SO/CH<sub>2</sub>Cl<sub>2</sub> (3:1). The solution was poured into ether, and the resulting precipitate was isolated by centrifugation to yield trideca-1,3,5,8,10,12-hexaenyl-1,13-bis(*N*-methyl-4-pyridinium) diiodide (DPy13-H) as a yellow solid (182 mg, 85%). <sup>1</sup>H NMR (Me<sub>2</sub>SO): 8.87 (2H, d,  $J = 6.6$  Hz), 8.75 (2H, d,  $J = 6.8$  Hz), 7.72 (1H, dd,  $J = 15.4$  Hz; 11.0 Hz), 6.88–6.33 (10H, m), 5.98 (1H, m), 4.27 (3H, s), 4.19 (3H, s), 3.76 (2H, d,  $J = 7.1$  Hz). IR (KBr pellet, cm<sup>-1</sup>): 2966.7, 1650.5, 1597.8, 1104.2, 1031.8, 808.0.

Trideca-1,3,5,8,10,12-hexaenyl-1,13-bis(*N*-methyl-4-pyridinium) diiodide (120 mg, 0.200 mmol) was dissolved in 3 mL of 2:1 Me<sub>2</sub>SO/CH<sub>2</sub>Cl<sub>2</sub>. 1,4-Diazabicyclo[2.2.2]octane (0.34 g, 3.0 mmol) in Me<sub>2</sub>SO (2 mL) was added dropwise. The deep blue-green solution was stirred at room temperature for 2 min and then poured into ether with vigorous stirring. The dark precipitate was filtrated and washed with ether. Attempts to purify this dark solid using chromatography failed due to the extreme sensitivity of the compound to oxygen. Spectral data for DPy13 were as obtained. <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>): δ 7.69 (4H, d,  $J = 6.2$  Hz), 7.21 (1H, t,  $J = 12.4$  Hz), 7.01 (4H, d,  $J = 6.2$  Hz), 6.70–6.55 (4H, m), 6.30–6.10 (6H, m), 5.90 (2H, d,  $J = 13.4$  Hz), 3.68 (6H, s). IR (KBr pellet, cm<sup>-1</sup>): 2966.7, 2927.2, 1729.4, 1643.9, 1485.9, 1466.2, 1110.8. UV-vis (DMSO): 738 nm (ca.  $1.7 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>).

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