Prototypes for the Polaronic Ferromagnet. Synthesis and Characterization of High-Spin Organic Polymers

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Received February 9, 1994[⊗]

Abstract: Preparation and characterization of several new polymers (**1–7**) that are considered one-dimensional prototypes for the polaronic ferromagnet are reported. Synthesis involved either Wittig or Suzuki coupling to produce polymers with extended π systems. Oxidative doping (I_2 or AsF_5) produces radical cations (polarons) that are stable at room temperature. Magnetic characterization of the doped polymers, using SQUID-based magnetometry, indicates that in several instances ferromagnetic coupling of polarons occurs along the polymer chain. Comparison of the various polymers reveals useful design principles and suggests new directions for the development of magnetic organic materials.

Introduction

Of the several strategies for developing organic-based magnetic materials,[1] the polaronic ferromagnet remains an appealing target. Early theoretical work by Fukutome[2] suggested that radical cations (polarons) obtained by oxidizing (doping) conjugated organic segments, when linked by appropriate π topologies, could serve as useful spin carriers of novel magnetic materials. In a different but equivalent parlance, the polaronic ferromagnet can be considered a realization of the schematic of Figure 1, which we[3–5] and others[1] have used to design and analyze novel high-spin and magnetic structures. In this scheme, a magnetic material is considered to consist of two types of building blocks; the spin-containing unit (SC) and the ferromagnetic coupling unit (FC), which ensures high-spin pairwise[6] interactions between SC's. In recent years there has been much work directed at evaluating potential FC's, and several good candidates exist. Of course, the defining feature of a polaronic ferromagnet is that the SC is a polaron.[8]

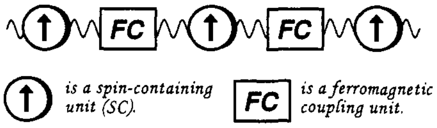

Figure 1. Schematic design for high-spin polymers. In the polaronic ferromagnet the SC is a polaron.

From our perspective, the polaronic ferromagnet has several attractive features. First, it is known from work on organic conducting polymers[9] that doped, conjugated organic molecules containing many polarons can be stable at room temperature. Thus, a polaron seemed a potentially "robust" SC. Second, the conducting polymer work also established that doping can be a fairly straightforward process, achieved chemically or electrochemically. Thus, the vexing problem of finding efficient ways to introduce a large number of spins into a system could be somewhat assuaged. Finally, many approaches to magnetic organic polymers produce intractable, insoluble materials that are very difficult to characterize.[10] The polaronic approach, as we have pursued it, separates the polymer synthesis step from the introduction of spins. Thus, one can fully characterize the polymer and firmly establish that the desired topology has in fact been created. Admittedly, the materials are more difficult to characterize after doping, a problem generally shared with the conducting polymers. Still, we do consider it an advantage that, at least at some level, the polymer is very well characterized.[11]

In the present work we describe our initial efforts directed toward the preparation of a polaronic ferromagnet.[5] In all systems described here, the FC is *m*-phenylene, the best characterized and perhaps most robust such unit.[1,3,7] In addition, we have considered only oxidative (p-type) doping to give radical cations as the SC's.[12] Our goals in these early systems were as follows:

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[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

(1) For recent overviews of this field, see: *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing Co.: Singapore, 1993; pp 415. *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991. *Ferromagnetic and High Spin Molecular Based Materials. Molecular Crystals and Liquid Crystals*; Miller, J. S., Dougherty, D. A., Eds.; Gordon and Breach Science Publishers: New York, 1989; Vol. 176; pp 1–562. *Chemistry and Physics of Molecular Based Magnetic Materials. Molecular Crystals and Liquid Crystals*; Iwamura, H., Miller, J. S., Eds.; Gordon and Breach Publishers: New York, 1993; Vol. 232, pp 1–360. Rajca, A. *Chem. Rev.* **1994**, *94*, 871–893.

(2) Fukutome, H.; Takahashi, I.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34–38.

(3) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *23*, 88–94.

(4) Dougherty, D. A. *Mol Cryst. Liq. Cryst.* **1989**, *176*, 25–32. Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618–7619.

(5) Preliminary reports on some aspects of this work have appeared: Dougherty, D. A.; Kaisaki, D. A. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 71–79. Dougherty, D. A.; Grubbs, R. H.; Kaisaki, D. A.; Chang, W.; Jacobs, S. J.; Shultz, D. A.; Anderson, K. K.; Jain, R.; Ho, P. T.; Stewart, E. G. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; pp 105–120. Dougherty, D. A.; Jacobs, S. J.; Silverman, S. K.; Murray, M.; Shultz, D. A.; West, A. P.; Clites, J. A. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 289–304.

(6) One can also consider FC's that couple three or more SC's into the highest possible spin state. A 1,3,5-trisubstituted benzene is such a structure.[7]

(7) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251–1259. Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J. *Chem. Lett.* **1992**, 369–372. Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872–874. Wasserman, E.; Schueller, K.; Yager, W. A. *Chem. Phys. Lett.* **1968**, *2*, 259–260.

(8) Technically, the radical cations involved here are not polarons, because they are not part of an infinite, conjugated polymer. By its very nature, the FC disrupts the conjugation. However, we feel the coinage of Fukutome[2] has descriptive value and so have adopted it.

(9) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 1, pp 1–726. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 2, pp 729–1417.

(10) For an overview, see: Miller, J. S. *Adv. Mater.* **1992**, *4*, 435–438.

(11) In principle, one can reverse the doping procedure to remake soluble, characterizable polymer. We have made only preliminary efforts along these lines. For I_2-doped **6**, treatment with $Na_2S_2O_3$ produces a soluble, pale-yellow material with UV spectra that are quite similar, but not identical, to those of the initial polymer. Similar treatment of I_2-doped **1** or **3** did not solubilize a significant amount of material.

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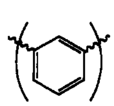
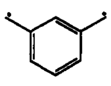


m-phenylene



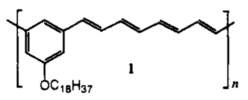
m-xylylene

to establish synthetic strategies for potential polaronic ferromagnets; to develop doping protocols and characterization procedures for the doped polymers; and to evaluate different SC's or, put differently, to determine which conjugated segments are best suited to producing a large number of spins that interact strongly through the FC.

It should be emphasized from the start that all the systems described here are inherently one-dimensional and so cannot be expected to spontaneously order into a bulk ferromagnet.[13] As such, the materials prepared are essentially paramagnets, and the magnetic characterization seeks evidence for short-range, high-spin ordering consistent with the scheme of Figure 1. At this early stage of the project, however, these simpler, one-dimensional systems can be easier to interpret and control than more complex, three-dimensional structures.

Design Criteria

Our initial targets are polymers **1–7**. Here, we will briefly lay out the issues that need to be considered in selecting a potential polaronic SC. It will become apparent that the conflicting demands placed on the system suggest that the optimal SC will embody a delicate balance of several factors.



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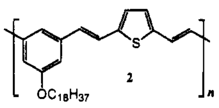

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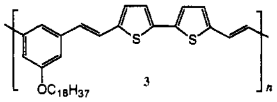

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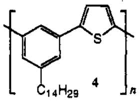

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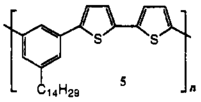

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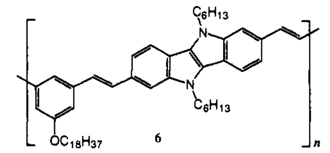

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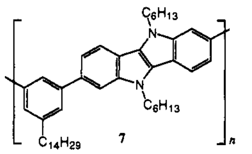

7

Our initial consideration focused on the minimal conjugation length that would be amenable to doping under mild conditions. In particular, we wished to be able to use I_2 (gas, or in solution) as a dopant, rather than the more caustic AsF_5. There was some indication from the conducting polymer literature that a segment as short as a triene could be doped with I_2.[14] This likely establishes a lower limit to polaron size.

While six carbons may represent a minimal polaron length, a number of factors contribute to establishing the optimal length. First, one wants the polaron to be as chemically inert as possible. Stabilizing a radical cation suggests increasing delocalization, and so a longer polaron would seem to be better. Introduction of heteroatoms and steric protection are additional strategies for producing stable radical cations.

However, two factors operate to favor shorter polarons. First is the formation of bipolarons. In conducting polymers, it is well established that, under conditions of heavy doping, polarons can be replaced by bipolarons, formed either by combination of two polarons or further doping of a polaron.[9,15] Either way, a bipolaron is a *spinless* dication[16] and is thus quite detrimental to the polaronic ferromagnet design. It seems safe to assume that, for a short enough dopable segment, bipolaron formation should be disfavored due to the Coulombic repulsions inherent in a dication.

The second factor that would appear to favor a shorter polaron is based on considerations of the potential effectiveness of the FC. Consider *m*-phenylene as an FC. The simplest high-spin system is the biradical *m*-xylylene, for which the triplet state is more stable than the singlet by ca. 10 kcal/mol.[17] However, it seems reasonable to assume that the magnitude of the high-spin preference will be diminished if the spin density at the benzylic centers is reduced. There are very few experimental tests of such reasoning, but in one case we recently studied,[18] spin-coupling strength did quantitatively scale with spin density at the "radical centers" of the FC. If one assumes that the spin is roughly equally delocalized over the length of a polaron,[19] then a longer polaron will "dilute" the spin and so could diminish the effectiveness of the FC.

Another factor that contrasts polaronic ferromagnets and conducting polymers is the degree of doping required. For conducting polymers, fairly light doping levels are often adequate. However, it seems likely that very high doping levels will be required to achieve spin concentrations that could lead to significant magnetic effects. This places a different set of constraints on the dopant/SC combination, emphasizing the ability to produce a large number of polarons without completely degrading the polymer.

It is well established from the conducting polymer field that long, planar, conjugated π systems are notoriously insoluble and so difficult to characterize. There are a number of potentially magnetic organic polymers that are intractable, insoluble, ill-characterized materials.[10] While these may become technologically important, they are poor vehicles for detailed structure–activity studies and thus for developing an *understanding* of the magnetic properties of the systems. Again, by analogy to work from the conducting polymer field, we reasoned that the inclusion of long alkyl chains would improve the solubility characteristics of the polymers. As described below, this indeed is the case. In this context, an especially attractive feature of *m*-phenylene as the FC becomes apparent. The 5 position (considering the 1 and 3 positions as connected to the polymer backbone) is ideal for introducing solubilizing groups. Even a very bulky substituent at the 5 position should not interfere with the polymer backbone. With conducting topologies, introduction of solubilizing groups often causes steric interference that leads to twisting out of conjugation along the polymer backbone. There will be a trade-off, as the introduction of solubilizing groups will dilute the material in terms of spins/g, but in these prototype systems, we have leaned toward maximizing solubility and hence characterizability. It has also been proposed that long alkyl chains could lead to ordering in a high-spin system and thereby promote favorable intermolecular interactions,[20] and this seems possible with these systems.

Target Structures and Synthetic Strategies

On the basis of the above considerations and another critical design issue—synthetic feasibility—we have targeted polymers

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[12] The alternative is reductive (n-type) doping to give radical anions. Studies of several n-type systems are underway in our labs.

[13] Mattis, D. C. *The Theory of Magnetism I*, 2nd ed.; Springer-Verlag: New York, 1988.

[14] Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894–896. Pranata, J.; Dougherty, D. A. *Synth. Met.* **1987**, *22*, 171–178. The triene in this polymer is stabilized by methyl substituents.

[15] Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309–315.

[16] Chemists must remember that we are discussing the solid state, not the gas phase. Coulombic repulsions in a bipolaron are considerably shielded by the solid environment and by the presence of counterions.

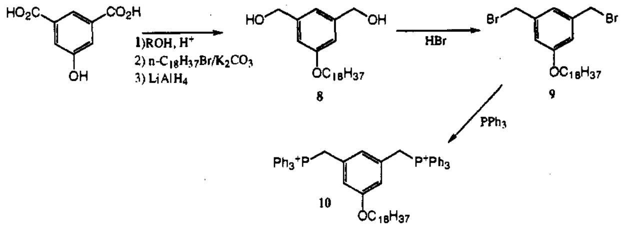
[17] Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791–1795.

[18] Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744–1753.

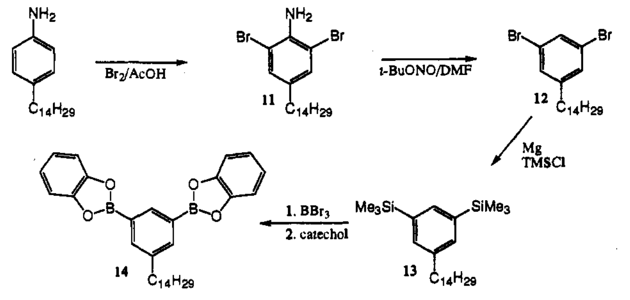
[19] In fact, spin density is not uniform across a polaron,[2] but certainly the absolute spin density is less at the end of a longer polaron.

[20] Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293–5294.

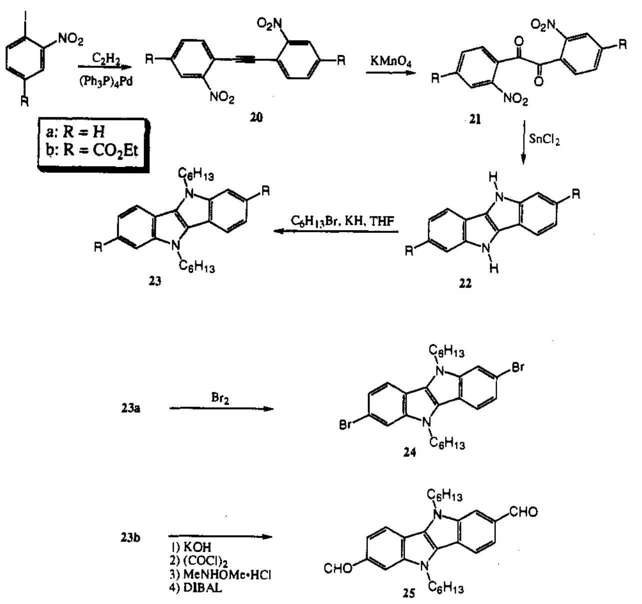
Scheme 1

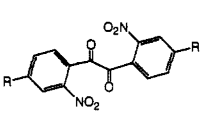


Scheme 2



Scheme 3



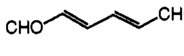


1–7 for these initial studies. We refer to these as derivatives of poly(*m*-phenylene) (PMP). In **1**, the additional unit is an octatetraene (OT), and so **1** is PMPOT. Other building blocks are 2,5-thiophene (T), 1,2-vinylene (V), and 2,7-indoloindole (I), and so the polymers are PMPVTV (**2**), PMPVTTV (**3**), PMPT (**4**), PMPTT (**5**), PMPVIV (**6**), and PMPI (**7**). One can also designate the solubilizing group. For example, we have studied both PMPOT-6[5] and PMPOT-18, which have, respectively, hexyl and octadecyl solubilizing groups. In the present work, however, we will only discuss the extract structures **1–7** and so will not add further descriptors.

We have used two different polymerization reactions: a Wittig reaction (**1**, **2**, **3**, **6**)[21] and a Pd-mediated Suzuki-type coupling (**4**, **5**, **7**).[22] Scheme 1 shows the synthesis of the *m*-phenylene component for the Wittig approach, starting from the commercially available hydroxyisophthalic acid. The hydroxy group provides a convenient point for attachment of the solubilizing alkyl chain. Initial studies established that a hexyl group was only moderately effective in this role.[5] However, an octadecyl group greatly increased solubility, and so it was used throughout. Standard chemistry produced the bisphosphonium salt **10**, which was used in the polymerization.

The *m*-phenylene component for the Suzuki polymerization was prepared as shown in Scheme 2. The commercially available 4-tetradecylaniline provided convenient access to a solubilizing alkyl chain and a directing group to provide the desired *meta* functionality. Again, fairly conventional chemistry produced the bis(boronic ester) **14**, which was used directly in polymerizations. Note there is a subtle difference between the polymers **1**, **2**, **3**, and **6** vs **4**, **5**, and **7**. In the former class the solubilizing group is octadecyloxy, while in the latter it is tetradecyl. The difference in chain length should not be an issue, but the presence of the oxygen could, in principle, be. Given its *meta* position, the oxygen should not have a large influence on polaron stability. However, the alkyl aryl ether is a potentially reactive site, especially with a strong oxidant/electrophile such as AsF_5.

Wittig polymerizations required appropriate dialdehydes for reaction with **10**. The precursor to polymer **1**, *trans,trans*-muconic aldehyde (**15**), was prepared by modification of a published procedure.[23] The thiophene dialdehydes **16** and **17** were readily prepared from known precursors.[24,25] Similarity, the thiophene dibromides **18** and **19** necessary for Suzuki couplings were readily available.[26]



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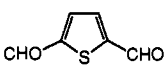

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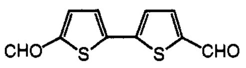

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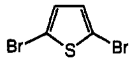

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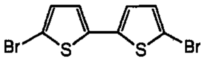

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The required indoloindole building blocks were prepared as shown in Scheme 3. The acetylene coupling chemistry shown constitutes a significant improvement over previous routes to such structures. Ring closure was then accomplished according to literature procedures.[27,28] N-Alkylation[27d] with *n*-hexyl bromide provided additional solubility and protected the reactive N–H functionality. Dibromide **24**, for use in Suzuki coupling, was prepared by direct bromination of **23a**. The Wittig component, dialdehyde **25**, was prepared by converting the esters[28] to aldehydes via the Weinreb amides.

The final polymerizations then proceeded as in Scheme 4. For all systems, polymers in the ca. 10 000 molecular weight range

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(21) McDonald, R. N.; Campbell, T. W. *J. Am. Chem. Soc.* **1960**, *82*, 4669–4671. Kossmehl, G.; Härtel, M.; Manecke, G. *Macromol. Chem.* **1970**, *131*, 15. Gourley, K. D.; Lillya, C. P.; Reynolds, J. R.; Chien, J. C. W. *Macromolecules* **1984**, *17*, 1025. Yen, K. Y.; Cava, M. P.; Huang, W. S.; MacDiarmaid, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, *1502*.

(22) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. Rehähn, M.; Schlülter, A. D.; Wegner, G.; Feast, W. I. *Polymer* **1989**, *30*, 1060–1062. Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592–4593.

(23) (a) Davies, S. G.; Whitmam, G. H. *J. Chem. Soc., Perkin Trans 1* **1977**, 1346–1347. (b) Kossmehl, G.; Bohn, B. *Chem. Ber.* **1974**, *107*, 710–711.

(24) Sone, T. *Bull. Chem. Soc. Jpn.* **1964**, *37* (8), 1197–1200.

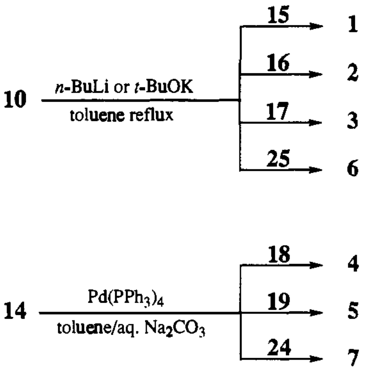
(25) Nakayama, J.; Fujimori, T. *Sulfur Lett.* **1990**, *11* (1 + 2), 29–30.

(26) Rutherford, D. R.; Stille, J. K.; Elliot, C. M.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294–2306.

(27) (a) Ruggli, P. *Chem. Ber.* **1917**, *50*, 883. (b) Heller, G. *Chem. Ber.* **1917**, *50*, 1202. (c) Ruggli, P. *Helv. Chim. Acta* **1938**, *18*, 845. (d) Hünig, S.; Steinmetzer, H.-C. *Liebigs Ann. Chem.* **1976**, 1090.

(28) Kaszynski, P.; Dougherty, D. A. *J. Org. Chem.* **1993**, *58*, 5209–5220.

Scheme 4



were prepared. These are quite acceptable values for step-growth polymerizations of this sort. The Wittig reaction, especially, is not generally considered ideal for obtaining high molecular weights, and we believe two factors work in our favor in these systems. First, great care was taken to ensure high purity for both components of the reaction and the solvent, as impurities will lead to chain termination. Second is the presence of effective solubilizing groups. Often, a polymerization of this sort will produce only oligomers because the growing chain falls out of solution. However, the long alkyl chains and the elevated reaction temperatures served to keep the growing polymer in solution, so that significant chain lengths could be achieved.

Doping Procedures. Both I_2 and AsF_5 were used as oxidative doping agents. Polymers **2**–**5** were doped with iodine at room temperature in tetrahydrofuran solution in a nitrogen-filled glovebox. For solubility reasons, **6** and **7** were doped in 1,1,1-trichloroethane and methylene chloride, respectively. Typically a 50% molar excess of dopant was added. For most polymers, the length of time the polymer was exposed to I_2 did not strongly influence its properties (but see below). The solvent was then removed and excess iodine removed under high vacuum. All I_2-doped polymers were dark in color and could not be redissolved in common organic solvents.

AsF_5 doping was performed at room temperature on a purpose-built vacuum line fitted with a pressure tranducer. To minimize rapid and inhomogeneous doping, polymer films (35–80-μm thick) were cast from $CHCl_3$ solution onto a Teflon block. Polymer **5** was doped as a loose powder due to its minimal solubility in organic solvents. Dry films/powders were placed in a tared vial and introduced into the doping chamber. The vacuum line was evacuated and thoroughly dried before a measured pressure of gas was introduced into the manifold. Excess dopant was removed under dynamic vacuum. We have studied a variety of doping conditions, but most studies involved one of two protocols. "Light doping" will refer to exposure to 50 Torr of AsF_5 for 30 min, whereas "heavy doping" will indicate exposure to 200–300 Torr for 5–7 h. The films became increasingly brittle as doping progressed.

Magnetic Characterization

As discussed above, it was anticipated that doping of polymers such as **1**–**7** would produce paramagnets, with no expectation of spontaneous ordering into a ferromagnet. In a paramagnet, one has a number of spin-containing species, and these do not interact with each other. The key question here is whether these spin centers are simply isolated polarons—monoradical cations with a spin value (S) of $^1/_2$—or whether there is some local high-spin coupling among several polarons to produce spin centers with $S > {}^1/_2$. For any paramagnet, a value of S can be obtained from a plot of magnetization (M) vs applied field (H). As the field increases, the induced moment increases until saturation occurs. At saturation, the moments of all the individual spin centers are aligned with the field, and so further increasing the field leads to no increase in M. The rate at which saturation is reached depends on the value of S, and such behavior can be quantitatively modeled by the Brillouin function.[29] We have developed quantitative fitting schemes that produce the optimal S value by fitting of a Brillouin function to the experimental data. The results of such studies are summarized in Table 1. Typical data sets and their fits to a Brillouin function are shown in Figure 2.[30]

Table 1. Values of S and Spin Concentration (in Parentheses) as Percent Monomers Doped[a]

polymer	I_2	AsF_5 light	AsF_5 heavy
PMPOT (**1**)	1.4 (0.6)[b]	2.2[c] (0.5)	0.5 (3.6)
PMPTV (**2**)	1.4 (0.8)	2.1[d] (0.2) 2.6[d] (0.2)[e]	0.5. (2.6)
PMPVTTV (**3**)	0.5 (2.2) 0.6[e]	0.6 (1.3)	0.6 (5.5)
PMPT (**4**)	[f]	0.6 (0.6)	0.6 (6.5)
PMPTT (**5**)	1.0 (1.0)	0.6 (8.8)[g]	0.7 (18.1)[g]
PMPIIV (**6**)	0.5–0.6 (16–17)	[h]	[h]
PMPII (**7**)	0.8 (32) 1.0 (32)[e]	[h]	[h]

[a] Measurements at 1.8 K unless noted otherwise. [b] Gas phase I_2 doping. Solution doping produces essentially identical results. [c] Values as high as 4.0 have been seen. [d] Values as high as 4.5 have been seen. [e] 4.5 K. [f] No significant moment. [g] Powder sample rather than film for AsF_5 studies. [h] Not performed.

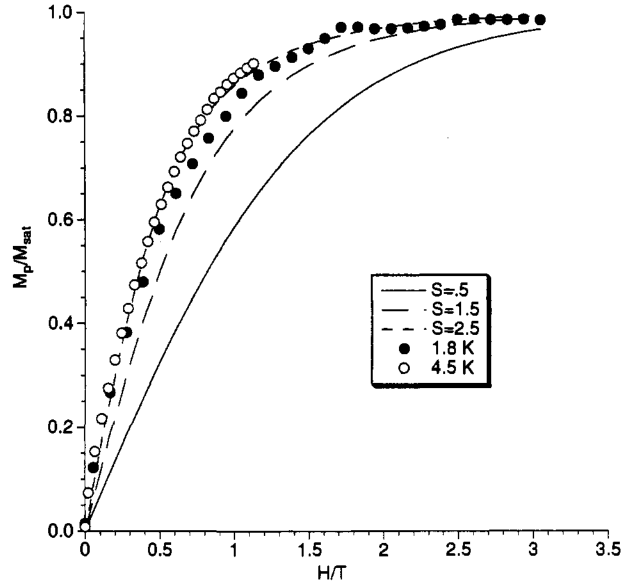


Figure 2. Typical magnetization saturation plot. Note ordinate is relative paramagnetic moment, normalized to M_{sat}. Data are for PMPVTV (**2**) under AsF_5/light doping conditions.

The other important quantity obtained from such studies is the saturation magnetization, M_{sat}, which is also obtained from the fit of the experimental data. This can be converted to an absolute spin concentration, thus providing an indication of the extent of doping. We will report these values as a percent of monomers doped. Technically, we are referring to the percent of monomers that contain a spin. Especially in the heavily doped samples, there is much more dopant uptake by mass than would be suggested by the value of M_{sat}. This could result from a number of factors, including bipolaron formation, cross-linking, and "clustering" of the doping agents (e.g., to form $As_2F_{11}^-$ or $As_3F_{16}^-$ counterions). Another factor that could effectively dimish M_{sat}, and hence the derived spin concentration, is the presence of antiferromagnetic interactions between polarons (see below).

PMPOT (1). Light doping with AsF_5 or I_2 doping produces S values that are unambiguously $> {}^1/_2$. Heavy doping with AsF_5

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(29) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986.

(30) For an overview of magnetic characterization of high-spin molecules, see: Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346–351.

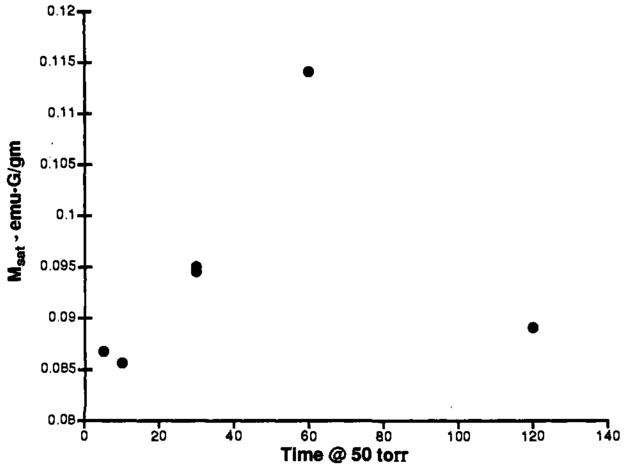

Figure 3. Variation of M_{sat} (from saturation plot) vs length of exposure to AsF_5 at 50 Torr for PMPOT.

leads to an increase in M_{sat}, but S is now $^1/_2$. Data at 4 K (AsF_5/light) generally indicate a larger S than data at 1.8 K.

With this polymer, we investigated several aspects of the doping procedure. For example, Figure 3 shows the variation in M_{sat}, which is an indication of the total number of spins, with the time of exposure to 50 Torr of AsF_5. There is a rise, followed by a turnover at longer exposures. We emphasize that there is some variability from run to run in such studies. Different samples can produce films of different thicknesses. Also, the doping process is inherently heterogeneous and so more prone to variation. Still, the basic pattern of Figure 3 is seen generally and is the basis for establishing the light-doping protocol.

Even under identical conditions, some variability is seen. For example, under the light-doping protocol, S values around 2.5 are most common, and S is never <2.0. However, in several samples significantly higher values were seen, and several samples gave S = 4.0.

In this polymer, and others, the AsF_5/light procedure generally produced higher S values than I_2 doping. However, the I_2 method is much more convenient and generally more reproducible. As such, in later polymers we emphasized the I_2 doping method.

As polyradicals go, these systems are fairly stable. For example, an AsF_5/light sample on storage for 5 days at room temperature under an inert atmosphere retained 70% of its original magnetization.

PMPVTV (2). This polymer is very similar to PMPOT. Both I_2 and AsF_5/light produce $S > {}^1/_2$, with the latter producing a larger S. Raising the temperature increases S, while AsF_5/heavy produces more spins but $S \approx 0.5$. As with the case of PMPOT; AsF_5/light generally produces S = 2.0–2.5 (Figure 2). However, S values as high as 4.5 have been seen in some samples. The doped polymer shows good thermal stability, with less than a 10% loss of spins after 7 days at room temperature (I_2).

PMPVTTV (3). Introducing the much larger dopable segment of PMPVTTV leads to two changes. The spin concentration increases significantly. However, in any state of doping, $S \approx 0.5$. The thermal stability of the doped polymer is similar to that of PMPVTV. However, unlike the cases of the other polymers, extending the I_2 doping time leads to a substantial *decrease* in spin concentration, with more than half the spins destroyed on extensive doping.

PMPT (4). The much shorter doping segment of PMPT gives rise to a polymer that cannot be doped by I_2. With AsF_5, significant spin concentrations are seen, but $S \approx 0.5$. In addition, after only 72 h at room temperature, most spins have decayed.

PMPTT (5). This polymer shows much higher spin concentrations, especially with AsF_5. However, this polymer is a powder sample rather than a film as for the other polymers. Dopant uptake is much more rapid for a powder, and so it is dangerous to compare the AsF_5 results (especially "light") for this system to the others. Only with I_2 doping is $S > {}^1/_2$ seen.

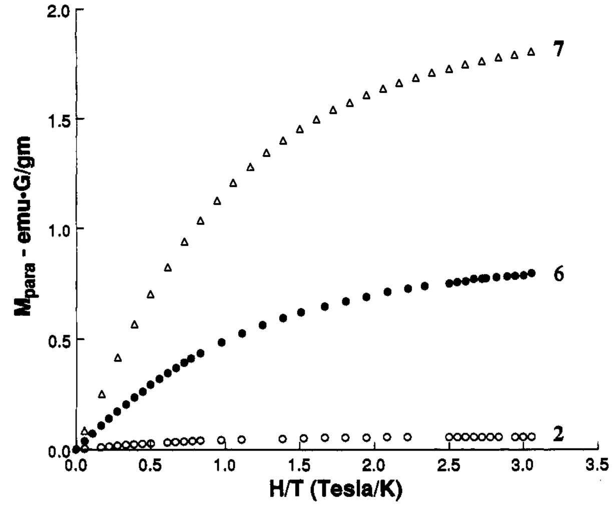

Figure 4. Saturation plots showing absolute paramagnetic moment in emu·G/g for comparably doped (I_2) **2**, **6**, and **7**.

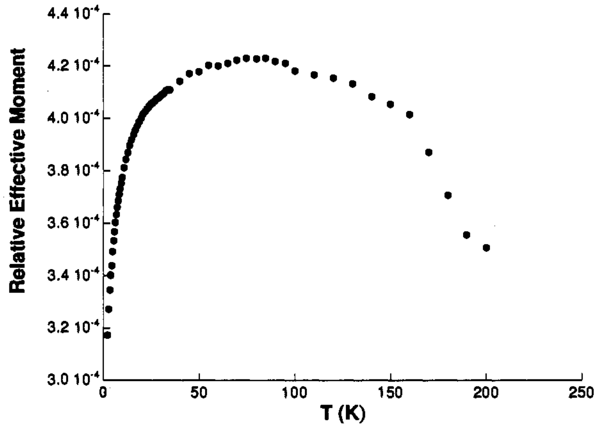

Figure 5. Typical relative effective moment plot. Data are for PMPVTV after AsF_5/light doping.

PMPVIV (6). Polymers with the indoloindole unit show very much higher spin concentrations. This dramatic difference is shown in Figure 4. However, with this system, $S \approx 0.5$.

PMPI (7). This polymer shows the highest spin concentrations for I_2 doping (Figure 4), with ca. one-third of the monomers containing a spin. In addition, S values are measurably $> {}^1/_2$. This system produces very stable spins, with no measurable loss in spin concentration after 7 days at room temperature.

Variable-Temperature Studies. When studied over a broad temperature range (2–200 K), all the doped polymers show the same qualitative behavior. This is illustrated in Figure 5. At intermediate temperatures, a roughly constant value of χT is seen, as expected for a paramagnet. However, there is a downturn in the effective moment as T drops below ca. 50 K. This is an indication of antiferromagnetic interactions and is seen in other high-spin solids. Also, consistent with this is the general increase in apparent S on raising the T of the saturation plots (Table 1, 1.8 vs 4.5 K).[31]

There is also a downturn in effective moment at elevated temperatures, again suggesting the onset of an antiferromagnetic interaction. There is some variation in the onset temperature for this phenomenon, but it is generally at temperatures between 100 and 200 K.

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(31) As expected from the plot of Figure 5, traditional Curie plots are not linear over the full temperature range. For samples with high enough spin concentrations so that strong signals can be obtained at high temperature, Curie plots from 50 to 200 K are linear and show small, negative θ values.

Discussion

These initial studies have provided some valuable insights into the strengths and weaknesses of the polaronic ferromagnet concept. Our initial target structure PMPOT produced very encouraging results, in that S values clearly $> {}^1/_2$ were seen. It also contained several weaknesses, most notably the very low spin concentration, which presumably arises, at least in part, from chemical instability of the polarons. Much of the work on polymers **2**–**7** represents efforts to improve upon the initial findings for PMPOT.

The thiophene-containing polymers provide several design clues. Our choice of thiophene was based on work in the conducting polymer area, where polythiophene and derivatives often have more desirable properties than polyacetylene (the polymer analogue of the OT fragment of PMPOT). We especially hoped that the heteroatom would stabilize the polarons, thereby producing a higher spin concentration.

PMPVTV (**2**) is structurally identical to PMPOT except there is a sulfur atom in each polyene chain. The sulfur seems to have little impact, and the two polymers have essentially identical magnetic properties.

Shortening the chain to produce PMPT (**4**) gives a polymer that cannot be doped by iodine. AsF_5 doping produces spins that are quite unstable, and we consider this polymer to define a structure that is too difficult to oxidize for our purposes. Expanding to the bithiophene unit to give PMPTT (**5**) again allows I_2 doping, and S is slightly $> {}^1/_2$. Further expansion to PMPVTTV (**3**) seems to have a detrimental effect. Spin concentration goes up for I_2 doping, but $S = 0.5$.

The indoloindole (**I**) unit was chosen because early studies by Hünig[27d] suggested it could give rise to very stable radical cations. We developed a new, general synthetic strategy this system and for all analogues in which the nitrogens are replaced by S and Se.[28] Electrochemical characterization of these systems, however, suggested that the parent **I** would be optimal. Structures such as these typically show two reversible oxidations below 1 V (vs $Ag^0/AgCl$).[27d,28] In contrast, short oligothiophenes typically show irreversible oxidations at significantly higher potentials.[32]

Incorporating the **I** unit does lead to a dramatic increase in spin concentration attainable with I_2 doping. A remarkable 32% of monomers support a spin upon I_2 doping of PMPI. Even at such high spin concentrations, an $S > {}^1/_2$ is seen.

Some comment on the meaning of the S values we obtain is in order. First, it must be appreciated that the value derived from the Brillouin fits is certainly an avarage from a complex mixture of sites.[33] While $S = 2.5$, for example, suggests five spins are interacting, it certainly does *not* mean that every spin in the system is part of a five-spin cluster. Were this so, the data would fit exactly to a Brillouin function, and this is never the case. It is easy to show that, for a mixture of S values, the saturation plots will be dominated by the larger S values at lower values of H/T and by the lower S values at higher field. Thus, when fit to a single Brillouin function, the low-field data should lie above the curve (implying a higher S) and the high field data should be below. We generally see such behavior in our fits.

The most important issue is not the exact value of S but rather that in several systems it is unambiguously greater than ${}^1/_2$. Such behavior is not seen in doped conducting polymers.[9,34] Nor is it typically seen in the many polymers that contain pendant radicals, with no rationally enforced spin-coupling pathway. Only when a high-spin topology is designed into a polymer does doping produce $S > {}^1/_2$.

Not only is it safe to assume that the S values we see represent an average for the material but it is also very likely that the spin distribution in these systems is extremely heterogeneous. For example, consider an AsF_5/light sample of PMPVTV. This gives $S \approx 2$–2.5, yet less than one of every 100 monomers is spin-containing. If the doping were homogeneous, very long-range spin correlations would be required. However, the molecular weights suggest that typical chains are 15-mers to 30-mers—on average there is less than one spin per chain! Given this, we believe that there are islands of heavy doping that can apparently produce large S values. Presumably, there are also many isolated, $S = {}^1/_2$ polarons, and the S we measure is an average of these two types of sites. The notion that doping does not produce homogeneous materials is common in the conducting polymer field[9] and is especially likely in two-phase systems such as gaseous AsF_5 interacting with polymer films. This may be why S values for AsF_5/light samples are generally higher than those for I_2 samples. Why such islands form is unknown, but one possibility is that the initial doping creates a polar environment which favors further doping nearby.[35]

Generally, in samples with $S > {}^1/_2$, the derived value of S increases as the temperature is raised from 1.8 to 4.5 K (Table 1, Figure 2). This is as expected, on the basis of the effective moment plot of Figure 5. This means that the S values we obtain at the very low temperatures are actually lower limits to the "true" value. That is, the measured values are diminished by the weak antiferromagnetic interactions that become evident below 50 K. It is a simple matter to estimate how big such an effect might be. Typically, the maximum value of $\mu_{\rm eff}$ ($\mu_{\rm eff}^{\rm max}$) is larger than the low-temperature value ($\mu_{\rm eff}^{\rm LT}$) by only about a factor of ${}^4/_3$. Since[29]

$$\mu_{\rm eff} = [g^2S(S+1)]^{1/2}$$

then

$$\frac{\mu_{\rm eff}^{\rm max}}{\mu_{\rm eff}^{\rm LT}} = \left[\frac{S^{\rm max}(S^{\rm max}+1)}{S^{\rm LT}(S^{\rm LT}+1)}\right]^{1/2} = 1.33$$

For a typical case with $S^{\rm LT} = 2.5$, one obtains $S^{\rm max} \approx 3.5$. This is a significant difference but not one that leads to any qualitative changes in interpretation.

The downturn in effective moment plots at $T < 50$ K (Figure 5) indicates weak, antiferromagnetic interactions in these materials. We, and others, have interpreted this to indicate *inter*molecular interactions. One would fully expect interchain interactions in these systems to be weak (and so manifest only at low T) and antiferromagnetic, consistent with our observations.[36]

It is more difficult to ascertain the interaction responsible for the high-temperature downturn in effective moment (Figure 5). One possible interpretation is that at these elevated temperatures the FC is no longer effective. That is, in this temperature regime kT is becoming comparable to the magnitude of the high-spin preference induced by the FC. Further work will be required to test this model.

Future systems should incorporate several features based on these results. The larger heterocycles TT and **I** seem to have been effective at allowing increased spin concentrations. Com-

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(32) (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728–2730. (b) Alemán, C.; Brillas, E.; Davis, A. G.; Fajarí, L.; Guo, D.; Juliá, L.; Perez, J. T.; Rius, J. *J. Org. Chem.* **1993**, *58*, 3091–3099. (c) Jen, K. Y.; Eckhardt, H. J.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, *215*–217. (d) Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B.; Van Phan, C.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021–1023.

(33) See, for example: Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688–10694.

(34) As controls, we have exposed both poly[(*p*-phenylene)vinylene] and poly[(*p*-phenylene)octatetraenylene] to standard doping conditions and characterized the doped polymers with the SQUID. In all cases, we see $S < {}^1/_2$. For details see: Kaisaki, D. A. Ph.D. Thesis, California Institute of Technology, 1990.

(35) We thank a reviewer for this suggestion.

(36) Recently, diamagnetic dimers of radical cations have been proposed as alternatives to bipolarons for oligothiophene systems. See ref 32a. Also, we have observed that the radical cations of the N-methyl derivative of **22b** are strongly antiferromagnetically coupled in the solid state. See ref 28.

parison of polymers **6** and **7** suggests that, once one has an adequately stable radical cation, introduction of a vinylene unit may be detrimental. That is, polymer **7** shows higher spin concentrations and higher S values than **6**. It could be that the vinylene unit is reactive, leading to overoxidation or cross-linking reactions. Alternatively, the vinylene polymer **6** should be more nearly planar, and this could enhance the antiferromagnetic interchain interactions.

There is a suggestion in the data of Table 1 that higher spin concentrations produce lower S values. We believe this could result from any of a number of factors. First, the AsF_5/heavy protocol almost certainly degrades polymers such as PMPOT and PMPVTV. One would expect a large amount of cross-linking, thereby destroying the designed topology and any hope of high spin coupling. These results provide strong support for our model that only polymers with the proper, designed topology will show $S > {}^1/_2$. Also, they rule out any role for impurities introduced by the doping agent, since samples with more AsF_5 show smaller S.

It is also true that the high spin concentration systems have more stable radical cations (i.e., lower oxidation potentials for the SC). It could be that in these systems the spin is, in effect, trapped on the SC and so spends little time on the FC. This could diminish spin–spin interactions. Perhaps it would be beneficial to more closely match the redox properties of the FC and the SC to encourage spin delocalization into the FC.[35]

Another effect of high spin concentration is a higher probability of interchain interactions. Since these are expected to be antiferromagnetic, they would lead to a diminution in the value of S determined by a Brillouin fitting. Clearly, future designs must address this issue. One strategy is to "insulate" the chains from one another by adding bulky groups. This could be useful for optimizing one-dimensional systems.

Ultimately, however, one should alter the interchain interactions so they become ferromagnetic rather than antiferromagnetic. Then, a true, three-dimensional system could develop. It is our belief that cross-linking is the optimal way to achieve this. It has long been recognized that not only is *m*-phenylene an FC but 1,3,5-trisubstituted benzenes can high-spin couple three SC's.[7] This presents an obvious strategy for high-spin cross-linking of polymer chains. Other approaches can be envisioned, and future studies from these labs will address these and other issues.

Experimental Section

Materials. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Toluene, methylene chloride, and trimethylsilyl chloride were distilled from CaH_2. 2,5-Dibromothiophene (**18**) was redistilled before use. All other starting materials were used as received.

Instrumentation. NMR spectra were recorded on a JEOL-GX 400 (399.65 MHz ^1H, 100.4 MHz ^{13}C) or a GE-300 spectrometer in $CDCl_3$ at room temperature and referenced to residual solvent protons unless specified otherwise. IR spectra were measured on a Perkin-Elmer 1600 instrument in a KBr pellet unless specified otherwise. Melting points were recorded on a Thomas Hoover melting point apparatus and are uncorrected. EI mass spectra, 70 eV, were obtained on a Hewlett-Packard 5890/5970 GC/MS. FAB and exact mass measurements were performed on a ZAB 7070 instrument at the University of California, Riverside. UV/visible spectra were recorded on a Beckman Instruments DU-640 continuous-wave spectrometer. Elemental analysis was determined at Atlantic Microlab, Norcross, GA, and Galbraith Laboratories, Knoxville, TN. Gel permeation chromatography was performed on a homemade instrument employing either three Shodex size Styragel columns (KF 803, KF 804, and KF 805) or an American Polymer Standards 10-μm mixed-bed column, an Altex model 110A pump, a Knauer differential refractometer, and a Kratos UV detector. Methylene chloride was used as an eluant at a flow rate of 1 mL/min. Molecular weights are reported relative to narrow polystyrene standards; polymer solutions (0.5% w/v) were passed through a 0.5-μm filter before injection.

Magnetization Studies. Variable-field and -temperature measurements were performed on a Quantum Design MPMS Squid Magnetometer. Samples were held in delrin screw-cap holders and loaded in the glovebox. Polymer samples were handled with Teflon-coated or plastic tweezers to avoid contamination by transition metals. The diamagnetic correction of the sample and holder, χ_{dia}, was determined from a plot of magnetic susceptibility, χ_e, vs inverse temperature. The correction may be estimated from the intercept upon extrapolation to infinite temperature. The plot was linear between 50 and 180 K. The magnetization of the sample was measured between 0 and 55 kG at constant temperature (1.8 or 4.5 K), starting with the high-field measurement to ensure saturation of ferromagnetic impurities throughout the curve. The spin states of the materials, S, were determined from a two-parameter Brillouin fit that simultaneously evaluates both S and the paramagnetic saturation moment M_{sat}. Variable-temperature behavior was determined between 2 and 300 K at constant field (usually 1 kG).

The spin concentration was evaluated most conveniently from the variable-field plot as follows: the experimentally determined saturation moment expressed in emu·G/g is converted to molar quantities by multiplying by the effective molecular weight, M^r, of the doped polymer's repeat unit. The molecular weight is compensated for dopant uptake:

$$M_{sat}\ (\text{emu·G/mol}) = M_{sat}\ (\text{emu·G/g}) \times M^r\ (\text{g/mol}) \qquad (1)$$

The saturation moment expected for a mole of molecules of spin S is described by

$$M_{sat}\ (\text{emu·G/mol}) = Ng\mu_\beta S \qquad (2)$$

where N is Avogadro's number, g is the Landé splitting factor, and μ_β is the Bohr magneton. Assuming $g = 2$, this can be written as

$$M_{sat}\ (\text{emu·G/mol}) = (1.117 \times 10^4)S \qquad (3)$$

Thus for $S = {}^1/_2$

$$\%\ \text{monomers doped} = 100\frac{M_{sat}\ (\text{emu·G/mol})}{(1.117 \times 10^4)0.5} \qquad (4)$$

Poly[(5-(Octadecyloxy)-*m*-phenylene)octatetraenylene] (1). To a stirring mixture of **10** (1.6723 g, 1.5821 mmol) in 10 mL of toluene contained in a Schlenk tube was slowly added 1.11 mL (3.17 mmol) of 2.8 M *n*-butyllithium (in hexanes) under argon. The red opaque mixture was stirred for 15 min at room temperature and then heated to 100 °C. To the stirring red bis-ylide mixture was added 0.1743 g (1.5829 mmol) of muconic aldehyde (**15**) dissolved in 10 mL of toluene at 100 °C via Teflon cannula. The addition took place over a 5-min period. The yellow mixture was stirred at 100 °C for 30 min and then refluxed for 72 h under argon. The mixture was allowed to cool to room temperature, and the solvent was removed by application of high vacuum. The remaining solid was purified using Soxhlet extraction with methanol (3 days). Solvent was removed by application of high vacuum, yielding 660 mg (93%) of yellow polymer. ^1H NMR δ 0.85 (m, 3 H), 1.28 (br, 28 H), 1.43 (br, 2 H), 1.78 (br, 2 H), 3.9 (br, 2 H), 6.4–6.8 (br, 11 H); IR (thin film) 680, 972, 998, 1465, 1568, 2852, 2922, 3018 cm^{-1}; GPC M_n = 6130, M_w = 15 800, PDI = 2.58, (MW of monomer = 449); UV ($CHCl_3$) λ_{max} = 400 nm, additional peak at 422 nm, sh at 382 nm. Anal. Calcd for $C_{32}H_{50}O$: C, 85.27; H, 11.18; O, 3.55. Found: C, 84.24; H, 10.72; O, 4.22; Br, 0.18; P, 0.27.

Poly[(5-(Octadecyloxy)-*m*-phenylene)vinylenethienylenevinylene] (2). Bisphosphonium salt **10** (3.5237 g, 3.3336 mmol) was added to a 100-mL Schlenk flask fitted with a magnetic stir bar. Toluene (20 mL) was added and the mixture stirred at room temperature for 20 min before 2.85 mL (6.67 mmol) of a 2.33 M *n*-BuLi solution in hexanes was added via syringe. The red opaque mixture was heated to reflux for 35 min. Dialdehyde **16** (0.4675 g, 3.334 mmol) dissolved in 20 mL of toluene was added via a Teflon cannula. The solution turned orange toward the end of the addition. The mixture was then refluxed under argon for 72 h. The solvent was then removed and the residue extracted with methanol for 72 h, yielding 1.2626 g (79%) of yellow polymer. ^1H NMR δ 0.86 (br, 3 H), 1.23 (br, 30 H), 1.75 (br, 2 H), 3.9 (br, 2 H), 6.5–7.4 (br, 9 H); IR (NaCl) 3016, 2922, 2851, 1582, 1465, 1299, 1167, 1057, 944, 850, 823 cm^{-1}; GPC M_n = 7040, M_w = 14 500, PDI = 2.06, (MW of monomer = 479); UV ($CHCl_3$) λ_{max} = 410 nm, additional peak at 436 nm. Anal. Calcd for $C_{32}H_{46}OS$: C, 80.28; H, 9.68; O, 3.34; S, 6.70. Found: C, 79.93; H, 9.91; O, 3.95; S, 6.76; P, <0.45; Br, <0.5.

Poly[(5-(Octadecyloxy)-*m*-phenylene)vinylenebithienylenevinylene] (3). Bisphosphonium salt **10** (1.5115 g, 1.4300 mmol), bisaldehyde **17** (0.3179 g, 1.430 mmol), and 20 mL of toluene were combined in a 50-mL Schlenk flask fitted with a stir bar. The mixture was stirred for 5 min. A solution of potassium *tert*-butoxide in THF (1.0 M, 4.4 mL) was then added dropwise, and the mixture went deep red in color. The solution was slowly warmed and refluxed under argon for 4 days. The brown mixture was then cooled and added to methanol (100 mL), yielding a brown solid. Soxhlet extraction with methanol yielded 420 mg (52%) of yellow-brown polymer. ^{1}H NMR δ 0.86 (br, 3 H), 1.23 (br, 30 H), 1.79 (br, 2 H), 3.9 (br, 2 H), 6.5–7.4 (br, 11 H); IR 3063, 3020, 2921, 2850, 1618, 1582, 1465, 1434, 1295, 1167, 1056, 943, 815, 786, 721, 678 cm^{-1}; GPC M_n = 9730, M_w = 12 710, PDI = 1.31, (MW of monomer = 561); UV ($CHCl_3$) λ_{max} = 432 nm, additional peak at 266 nm. Anal. Calcd for $C_{36}H_{48}OS_2$: C, 77.09; H, 8.73; O, 2.84; S, 11.43. Found: C, 77.16; H, 8.52; O, 3.17; S, 10.11; P, <0.4; Br, <0.05.

Poly[(5-tetradecyl-*m*-phenylene)thienylene] (4). 2,5-Dibromothiophene (**18**; 0.5402 g, 2.233 mmol), bisboronic ester **14** (1.1121 g, 2.1794 mmol), and $Pd(PPh_3)_4$ (30 mg) were combined in a 50-mL Schlenk flask in the glovebox. Toluene (20 mL) was added and the solution purged with argon. A deoxygenated, aqueous Na_2CO_3 (2 M, 5 mL) solution was then added and the heterogeneous mixture slowly brought to reflux under argon. The resulting yellow solution was refluxed for 72 h, cooled, and added to acetone (150 mL). The resulting filtrate was washed with 1% v/v HCl solution, extracted with hot toluene, and reprecipitated with acetone, yielding 348 mg (45%) of yellow polymer. ^{1}H NMR (CD_2Cl_2) δ 0.86 (br, 3 H), 1.23 (br, 22 H), 1.66 (br, 2 H), 2.65 (br, 2 H), 7.1–7.5 (br, 4 H), 7.5–7.8 (br, 1 H); IR 3071, 2851, 1592, 1466, 1376, 1238, 1095, 994, 862, 796, 721, 691 cm^{-1}; GPC M_n = 9510, M_w = 11 720, PDI = 1.23 (MW of monomer = 355); UV ($CHCl_3$) λ_{max} = 345 nm. Anal. Calcd for $C_{24}H_{34}S$: C, 81.30; H, 9.66; S, 9.04. Found: C, 80.56; H, 9.12; S, 8.39.

Poly[(5-tetradecyl-*m*-phenylene)-2,2′-bithienylene] (5). Dibromide **19** (0.5131 g, 1.651 mmol), bisboronic ester **14** (823.0 mg, 1.613 mmol), and $Pd(PPh_3)_4$ (22.9 mg) were added to a 50-mL Schlenk flask. Toluene (20 mL) and a solution of Na_2CO_3 (2 M, 4 mL) were added and the pale-yellow heterogeneous mixture purged with argon and warmed slowly to reflux temperature. The yellow solution was reluxed under argon for 72 h, allowed to cool to room temperature, and added to 150 mL of acetone. The resulting yellow precipitate was washed with warm water and extracted with ethanol and 1,1,1-trichloroethane. The high molecular weight fraction was extracted with xylenes and reprecipitated with methanol to yield 499 mg (71%) of yellow polymer. ^{1}H NMR ($CDCl_3$, 50 °C) δ 0.86 (br, 3 H), 1.25 (br, 22 H), 1.70 (br, 2 H), 2.66 (br, 2 H), 7.1–7.5 (br, 6 H), 7.6–7.7 (br, 1 H); IR 3068, 2921, 2849, 1588, 1452, 1364, 1235, 864, 791 cm^{-1}; GPC M_n = 7040, M_w = 7820, PDI = 1.11 (MW of monomer = 437); UV ($CHCl_3$) λ_{max} = 390 nm. Anal. Calcd for $C_{28}H_{36}S_2$: C, 77.01; H, 8.31; S, 14.68. Found: C, 77.81; H, 8.37; S, 14.76.

Poly[(5-(octadecyloxy)-*m*-phenylene)vinylene(5,10-dihexyl-5,10-dihydro-2,7-indolo[3,2-*b*]indolylene)vinylene] (6). A solution of potassium *tert*-butoxide in THF (1 M, 3.0 mL) was slowly added in a period of 5 min to a stirred suspension of vacuum-dried phosphonium salt **10** (1097.0 mg, 1.038 mmol) and dialdehyde **25** (446.8 mg, 1.038 mmol) in anhydrous toluene (20 mL) under an atmosphere of dry argon. The red color of the ylide disappeared immediately, and the salt began dissolving. The resulting reaction mixture was kept overnight at 50 °C and then at gentle reflux (oil bath) for the next 24 h. The resulting viscous, silty, and strongly fluorescent mixture was poured into ethanol (100 mL), and the yellow precipitate was filtered off. Crude product was extracted with ethanol overnight and then with benzene, and finally the higher fraction of the polymer was extracted with trichloroethane (35 mL). Ethanol (20 mL) was added to the last extract, and the resulting voluminous, yellow precipitate of the polymer was centrifuged and dried to yield 400 mg (52% yield) of brown-yellow solid. ^{1}H NMR (CD_2Cl_2) δ 0.88 (br, 9H), 1.26 (br, 42 H), 1.84 (br, 2 H), 2.00 (br, 4 H), 4.08 (br, 2 H), 4.49 (br, 4 H), 6.8–7.8 (br m, 13 H); IR 3024, 2922, 2852, 1630, 1582, 1466, 1235, 1162, 956, 848, 629 cm^{-1}; GPC M_n = 21 000, M_w = 31 000, PDI = 1.5 (MW of monomer = 769); UV (CH_2Cl_2) λ_{max} = 395 nm, additional peaks at 312, 440 nm. Anal. Calcd for $C_{54}H_{76}N_2O$: C, 84.32; H, 9.96; N, 3.64. Found: C, 84.37; H, 9.98; N, 3.62.

Iodine doping: Stirred overnight with excess of iodine in $C_2H_3Cl_3$; excess iodine was removed under high vacuum for several hours; resulting black polymer was vacuum dried. Anal. Calcd for $C_{54}H_{76}I_3N_2O$: C, 56.40; H, 6.66; I, 33.11; N, 2.44. Found: C, 59.74; H, 6.98; I, 29.25; N, 2.62.

Similarly, doping with 1 equiv of $NOBF_4$. Anal. Calcd for $C_{54}H_{76}BF_4N_2O$: C, 75.76; H, 8.95; N, 3.39. Found: C, 72.13; H, 9.86; N, 2.13.

Poly[(5-tetradecyl-*m*-phenylene)(5,10-dihexyl-5,10-dihydro-2,7-indolo[3,2-*b*]indolylene)] (7). A mixture of dibromide **24** (297.2 mg, 0.558 mmol), boronic ester **14** (284.8 mg, 0.558 mmol), benzene (10 mL), 2 M Na_2CO_3 (5 mL), and $Pd(PPh_3)_4$ (30 mg) was refluxed under argon atmosphere for 3 days. Water and CH_2Cl_2 were added, and the organic phase was separated, dried, filtered, and evaporated, leaving 0.40 g of glassy brown-yellow material. ^{1}H NMR (CD_2Cl_2) δ 0.88 (br, 9 H), 1.26 (br, 36 H), 1.81 (br, 2 H), 2.05 (br, 4 H), 2.85 (br, 2 H), 4.62 (br, 4 H), 7.4–8.0 (br m, 9 H); IR 3048, 2922, 2851, 1623, 1593, 1484, 1235, 1055, 908, 848, 798 cml–^{1}; GPC M_n = 4110, M_w = 16 030, PDI = 3.90 (monomer = 645); UV (CH_2CL_2) λ_{max} = 358 nm, additional peaks at 299, 387 nm. Anal. Calcd for $C_{46}H_{64}N_2$: C, 85.65; H, 10.00; N, 4.34. Found: C, 82.47; H, 9.26; N, 3.97.

5-(Octadecyloxy)benzene-1,3-dimethanol (8). A mixture of 5-hydroxyisophthalic acid (54.6 g, 0.300 mol), *n*-butanol (100 mL), and toluenesulfonic acid (1 g) was refluxed for 30 min. Benzene (100 mL) was added, the mixture was refluxed, and water was collected in a Dean–Stark trap. The mixture was evaporated and vacuum dried, and the resulting oily residue was dissolved in acetonitrile (400 mL) containing octadecyl bromide (100 g, 0.30 mol), anhydrous potassium carbonate (70 g), and tetrabutylammonium chloride (1 g). The mixture was stirred and refluxed overnight, diluted with hexanes, and filtered through Celite, and the salts were washed with hexane. The filtrate was evaporated, and the oily residue was dissolved in hexanes and filtered through silica gel. The concentrated yellowish filtrate was dissolved in ether (500 mL) and slowly added to a stirred suspension of $LiAlH_4$ (25 g) in ether (1000 mL). The mixture was refluxed for 3 h and decomposed by careful addition of ether saturated with water (500 mL), followed by water (30 mL), 15% NaOH (30 mL), and water (90 mL). The resulting white-gray suspension was filtered through Celite, and the salts were washed several times with hot THF. Combined organic phases were evaporated, and the white crystalline residue (103.4 g) was recrystallized from ethanol followed by recrystallization (hexane–benzene) to give 95.40 g (78% overall yield based on the diacid) of white crystals: mp 91–92 °C; ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3 H), 1.26 (br, 28 H), 1.41–1.49 (m, 2 H), 1.64 (t, J = 6.0 Hz, 2 H), 1.74–1.81 (m, 2 H), 3.97 (t, J = 6.5 Hz, 2 H), 4.67 (d, J = 6.0 Hz, 4 H), 6.85 (s, 2 H), 6.93 (s, 1 H); IR 3312, 2916, 2849, 1021 cm^{-1}; EIMS m/z 407 (M + 1, 27), 406 (M, 100), 154 (42). Anal. Calcd for $C_{26}H_{44}O_3$: C, 76.79; H, 11.40. Found: C, 76.74; H, 11.38.

1,3-Bis(bromomethyl)-5-(octadecyloxy)benzene (9). A slow stream of hydrogen bromide was passed overnight through a stirred suspension of diol **8** (5.00 g, 12.3 mmol) in benzene (50 mL). The resulting clear colorless solution was filtered through a silica gel plug, and the filtrate was evaporated to yield 5.35 g (82% yield) of white dibromide **9**. Recrystallization (hexanes) gave 4.70 g (72% yield) of white solid: mp 71–72 °C; ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25 (br, 28 H), 1.44–1.52 (m, 2 H), 1.75–1.80 (m, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.43 (s, 4 H), 6.85 (s, 2 H), 6.98 (s, 1 H); ^{13}C NMR δ 14.10, 22.67, 26.00, 29.17, 29.35, 29.55, 29.58, 29.65, 29.68, 31.91, 32.88, 68.18, 115.18, 121.54, 139.50, 159.56; IR 2918, 1850, 1328, 698 cm^{-1}; EIMS m/z 534 (50), 533 (27), 532 (100), 530 (50), 201 (31), 199 (30). Anal. Calcd for $C_{26}H_{44}Br_2O$: C, 58.65; H, 8.33; Br, 30.02. Found: C, 58.70; H, 8.33; Br, 29.90.

5-(Octadecyloxy)-1,3-bis((triphenylphosphono)methyl)benzene Dibromide (10). Triphenylphosphine (4.04 g, 15.4 mmol) and dibromide **9** (3.73 g, 6.98 mmol) were refluxed in dry acetonitrile (30 mL) under an atmosphere of dry argon overnight. The solvent was evaporated, and the white residue was vacuum dried, dissolved in chloroform, and precipitated from an ether–hexane mixture (5:1). The precipitation process was repeated twice, and the product was vacuum dried (12 h, 120 °C) to yield a white solid: mp 141–143 °C; ^{1}H NMR δ 0.87 (t, J = 6.5 Hz, 3 H), 1.17–1.40 (m, with maximum at 1.27, 32 H), 3.33 (t, J = 5.9 Hz, 2 H), 5.15 (d, J = 14.4 Hz, 4 H), 6.51 (s, 2 H), 7.05 (br s, 1 H), 7.61–7.66 (m, 12 H), 7.71–7.76 (m, 18 H); ^{13}C NMR δ 13.78, 22.32, 25.57, 28.49, 28.99, 29.03, 29.26, 29.30, 29.35 (3 C), 29.38 (3 C), 29.86, 31.56, 67.72, 117.22 (d, J = 86 Hz), 117.44, 126.16 (br), 129.01 (d, J = 11 Hz), 129.91 (d, J = 12.5 Hz), 134.15 (d, J = 10.3 Hz), 134.62, 158.43 (br); ^{31}P NMR δ 26.21 (s); FAB MS m/z 977 and 975 (M – Br, 7), 896 (73), 895 (100), 634 (21), 262 (32), 183 (42). Anal. Calcd for $C_{62}H_{74}P_2Br_2O$: C, 70.45; H, 7.06; O, 1.51; P, 5.86; Br, 15.12. Found: C, 70.79; H, 7.06; O, 0.90; P, 5.97; Br, 15.16.

2,6-Dibromo-4-tetradecylaniline (11). 4-Tetradecylaniline (25.0 g, 86.4 mmol) was dissolved in acetic acid (250 mL), and bromine (28.0 g, 173 mmol) was slowly added at room temperature. The white thick suspension was stirred overnight and poured into water, and the precipitate was filtered off. The crude product was recrystallized from 2-propanol to yield 35.4 g (91% yield) of pale crystals: mp 78–80 °C; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3 H), 1.25 (br, 22 H), 1.50–1.56 (m, 2 H), 2.44 (t, J = 7.5 Hz, 2 H), 4.38 (br s, 2 H), 7.19 (s, 2 H); ^{13}C NMR δ 14.12, 22.69, 29.08, 29.35, 29.42, 29.54, 29.65 (2 C), 29.68 (2 C), 31.40, 31.92, 34.41, 108.72, 131.53, 134.61, 139.63; IR 3432, 3342, 2952, 2918, 2846, 1617, 1577, 1543, 1468, 864, 732, 712 cm^{-1}; EIMS *m/z* 449 (53), 447 (100), 445 (50), 266 (33), 264 (69), 262 (34). Anal. Calcd for $C_{20}H_{33}Br_2N$: C, 53.70; H, 7.44; Br, 35.73; N, 3.13. Found: C, 53.75; H, 7.44; Br, 35.65; N, 3.14.

1,3-Dibromo-5-tetradecylbenzene (12). The dibromoaniline **11** (35.0 g, 78.3 mmol) was slowly (45 min) added to a stirred warm mixture of DMF (55 °C, 350 mL) and *tert*-butyl nitrite (90%, 20 g) under a blanket of argon. The resulting brown-yellow solution was stirred for 30 min, cooled down, and poured into 1% hydrochloric acid. The product was extracted twice with hexanes, and the organic phase was dried and filtered through a silica gel plug. The almost colorless filtrate was evaporated, and the resulting residue was Kugelrohr distilled (210 °C/0.2 Torr). The yellowish distillate was dissolved in pentane and filtered through silica gel, and the filtrate was evaporated to yield 23.62 g of 90% pure (by GC) dibromide. Analytical sample was obtained by recrystallization of the crude product from ethanol–hexane: mp 38 °C; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3 H), 1.25 (br, 22 H), 1.53–1.59 (m, 2 H), 2.53 (t, J = 7.5 Hz, 2 H), 7.25 (d, J = 1.7 Hz, 2 H), 7.47 (t, J = 1.7 Hz, 1 H); ^{13}C NMR δ 14.12, 22.69, 29.12, 29.36, 29.38, 29.50, 29.62, 29.65 (2 C), 29.68, 29.69, 31.01, 31.92, 35.37, 122.66, 130.26, 131.27, 146.88; IR 2925, 2853, 1585, 1553, 1420, 849, 741 cm^{-1}; EIMS *m/z* 434 (32), 432 (62), 430 (31), 252 (51), 250 (100), 248 (53). Anal. Calcd for $C_{20}H_{32}Br_2$: C, 55.57; H, 7.46; Br, 36.97. Found: C, 55.54; H, 7.43; N, 37.08.

1,3-Bis(trimethylsilyl)-5-tetradecylbenzene (13). Mg turnings (2.601 g, 0.111 mol), THF (15 mL), and trimethylsilyl chloride (13.696 g, 0.1261 mol) were stirred in a 250-mL, three-necked flask fitted with a reflux condenser and an addition funnel. The Grignard reaction was activated by the addition of a few drops of dibromoethane, and dibromide **12** (21.30 g, 0.0493 mol) dissolved in 50 mL of THF was slowly added over a 1-h period. The resulting red solution was refluxed under argon for 18 h. The mixture was then cooled, added to hexane (150 mL), and washed with saturated NH_4Cl solution (100 mL). The aqueous layer was further extracted with 2 × 50 mL of hexane, and the combined organic extracts were passed through 2-in. of silica gel. Concentration yielded 11.47 g of crude (79% pure by GC/MS) product. The sample may be further purified (>95%) by vacuum distillation (bp 170 °C/55 mTorr). ^{1}H NMR δ 0.27 (s, 18 H), 0.86 (t, J = 6.8 Hz, 3 H), 1.25 (br, 22 H), 1.61 (br m, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 7.33 (s, 2 H), 7.49 (s, 1 H); ^{13}C NMR δ –0.99, 14.16, 22.74, 29.42, 29.57, 29.61, 29.70, 29.74, 31.88, 31.98, 36.33, 134.06, 135.50, 139.25, 141.12; EIMS *m/z* 418 (M, 11), 404 (38), 403 (M – 15, 100), 329 (12), 221 (9), 73 (95).

5-Tetradecyl-1,3-phenylenebis(1,3,2-benzodioxaborole) (14). Crude 1,3-Bis(trimethylsilyl)-5-tetradecylbenzene (**13**; 803 mg, 1.92 mmol) was dissolved in methylene chloride (10 mL) and the solution cooled to –78 °C. A solution of BBr_3 in methylene chloride (1.0 M, 3.8 mL) was slowly added with stirring. The resulting pale-yellow suspension was then allowed to slowly warm to room temperature and refluxed for 24 h under argon. The red solution was cooled in an ice bath, and catechol (0.423 g, 3.84 mmol) was added in one portion. The white suspension was stirred at room temperature for 24 h and filtered. The filtrate was redissolved in methylene chloride and passed through a short column of neutral alumina. Recrystallization from chloroform afforded 496 mg (50.7%) of pure bisboronic ester: mp 144–145 °C; ^{1}H NMR δ 0.87 (t, J = 6.8 Hz, 3 H), 1.25 (br, 22 H), 1.71 (br m, 2 H), 2.75 (t, J = 7.8 Hz, 2 H), 7.15 (dd, J = 3.4, 2.4 Hz, 4 H), 7.35 (dd, J = 3.4, 2.4 Hz, 4 H), 8.10 (s, 2 H), 8.66 (s, 1 H); ^{13}C NMR (50 °C) δ 14.02, 22.68, 29.36, 29.40, 29.53, 29.62, 29.69, 31.50, 31.95, 35.95, 112.61, 122.83, 125.88 (br, C–B), 138.86, 139.36, 142.62, 148.71; IR 3033, 2918, 2872, 1600, 1473, 1454, 1397, 1303, 1235, 1136, 914, 863, 811, 741, 706 cm^{-1}; FAB *m/z* 510 (M, 4), 327 (12), 235 (8), 209 (11), 137 (13), 136 (100), 121 (10), 120 (21); HRMS 510.3105, calcd for $C_{32}H_{40}B_2O_4$ 510.3113. Anal. Calcd for $C_{32}H_{40}B_2O_4$: C, 75.32; H, 7.90; B, 4.24. Found: C, 75.35; H, 7.96; B, 4.16.

Muconic Aldehyde (15). This method is a modified version of the Kossmehl synthesis.[23] In a 250-mL round-bottom flask was added glyoxal trimeric dihydrate (1.408 g, 0.0201 mol) and dimethylformamide (80 mL). The mixture was heated to 80 °C under argon for 8 h. The dark-brown mixture was allowed to cool to room temperature and the solvent evaporated to give a dark-brown solid. This crude product was dissolved in 200 mL of benzene and gravity filtered. The filtrate was passed through a short column (2 in.) of silica with 800 mL of benzene. The solvent was evaporated, and the resulting brown solid was further purified by two successive flash chromatography columns using 7:3:2 petroleum ether–benzene–ethyl acetate eluent system. The second purification used an air-sensitive chromatography column, with collection of the product fractions under inert atmosphere conditions. The solvent was evaporated under vacuum in the absence of light to give the final product which was transferred into the drybox and used immediately. The product may also be purified by recrystallization from $CHCl_3$–pentane under an inert atmosphere. This yielded 490 mg (4.45 mmol, 22%) of light-yellow crystals: ^{1}H NMR δ 6.57 (m, 2 H), 7.30 (m, 2 H), 9.73 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 137.96, 146.28, 192.29.

2,5-Thiophenedicarbaldehyde (16) was prepared by Kröhnke oxidation of 2,5-bis(chloromethyl)thiophene:[24] mp 114.5–115.5 °C; ^{1}H NMR δ 7.84 (s, 2 H), 10.04 (s, 2 H); ^{13}C NMR δ 134.83, 149.24, 183.25. Anal. Calcd for $C_6H_4SO_2$: C, 51.42; H, 2.88. Found: C, 51.22; H, 2.94.

2,2′-Bithiophene-5,5′-dicarbaldehyde (17).[25] 2,2′-Bithiophene (1.124 g, 6.760 mmol) was dissolved in diethyl ether (35 mL) and the solution cooled to –5 °C. A solution of *n*-BuLi in hexanes (2.5 M, 5.5 mL) was added dropwise via a syringe. The cloudy mixture was slowly allowed to rise to room temperature and refluxed under argon for 90 min. Anhydrous dimethylformamide (1.134 g, 15.51 mmol) dissolved in THF (35 mL) was then added at 0 °C, and the reactants were stirred at room temperature overnight, added to HCl (10%, 200 mL), and neutralized with sodium bicarbonate. Filtration yielded a crude brown solid which was recrystallized from chloroform (twice) and sublimed at 170 °C/20 mTorr: Yield = 776 mg (52%); mp 213–214 °C (lit.[25] mp 215–216.5 °C); ^{1}H NMR δ 7.40 (d, J = 4.0 Hz, 2 H), 7.71 (d, J = 4.0 Hz, 2 H), 9.90 (s, 2 H); ^{13}C NMR δ 126.47, 136.89, 143.86, 144.82, 182.53. Anal. Calcd for $C_{10}H_6S_2O_2$: C, 54.04; H, 2.72; S, 28.85. Found: C, 54.03; H, 2.70; S, 28.75.

2,2′-Dinitrotolane[37] **(20a). Method A.** Pure acetylene was slowly bubbled through a stirred degassed solution of 2-iodonitrobenzene (62.5 g, 0.25 mol), $(Ph_3P)_4Pd$ (0.80 g), and CuI (0.80 g) in a mixture of dry triethylamine (250 mL) and pyridine (250 mL). After 2 days the resulting precipitate was filtered, washed with water, dried, dissolved in chloroform, and passed through a silica plug. The yellow filtrate was evaporated, and the residue (26.22 g) was recrystallized (toluene) to give 24.45 g (73% yield) of long yellow needles. **Method B.** 2-Iodonitrobenzene (24.9 g, 0.10 mol) was dissolved in dry triethylamine (200 mL), the solution was purged with argon, and $(Ph_3P)_2PdCl_2$ (100 mg) and CuI (25 mg) were added, followed by (trimethylsilyl)acetylene (15.5 mL, 0.11 mol). The mixture was stirred for 5 h, hexanes were added, and the suspension was filtered through a silica plug. The resulting yellow eluate was evaporated, the oily residue was dissolved in methanol (50 mL), and a solution of KOH in methanol (10%, 50 mL) was slowly added. The resulting dark mixture was stirred for 1 h and poured into water.[38] The product was extracted with ether, dried, and filtered through a silica plug. The solvent was evaporated, the resulting crude (2-nitrophenyl)acetylene was dissolved in triethylamine (300 mL) containing 2-iodonitrobenzene (23.0 g), the solution was purged with argon, and $(Ph_3P)_2PdCl_2$ (100 mg) and CuI (25 mg) were added. The mixture was stirred overnight, and the resulting yellow precipitate was collected by filtration and dissolved in ethanol. The ethanol solution was boiled, cooled, and filtered to give crude product which was recrystallized (toluene) to give 13.67 g (51% yield) of pale-yellow needles: mp 186–189 °C dec (lit.[37] 189–189.5 °C); ^{1}H NMR δ 7.51–7.56 (m, 2 H), 7.63–7.68 (m, 2 H), 7.82 (d, J = 7.8 Hz, 2 H), 8.14 (d, J = 8.3 Hz, 2 H); ^{13}C NMR δ 91.96, 118.06, 124.82, 129.54, 133.13, 135.26, 149.47; IR 1569, 1522, 1342, 746 cm^{-1}; CIMS (NH_3) *m/z* 286 (M + NH_4, 100), 134 (31).

Diethyl 2,2′-Dinitrotolane-4,4′-dicarboxylate (20b). The tolane was prepared as described for **20a** in Method A from ethyl 4-iodo-3-nitrobenzoate[39] obtained in 78% yield from 4-iodobenzoic acid: mp 205 °C dec; ^{1}H NMR δ 1.45 (t, J = 7.1 Hz, 6 H), 4.46 (q, J = 7.1 Hz, 4 H), 7.91 (d, J = 8.1 Hz, 2 H), 8.31 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 2 H), 8.78 (d, J = 1.5 Hz, 2 H); ^{13}C NMR δ 14.22, 62.18, 93.89, 121.27, 125.85, 132.16, 133.48, 135.44, 149.48, 163.81; IR 1712, 1529, 1346, 1282, 1235 cm^{-1}; CIMS *m/z* 430 (M + NH_4, 100), 206 ($^1/_2$M, 66). Anal. Calcd for $C_{20}H_{16}N_2O_8$: C, 58.25; H, 3.91; N, 6.795. Found: C, 58.27; H, 3.89; N, 6.86.

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(37) Klieg, A.; Haas, K. *Chem. Ber.* **1911**, *44*, 1209.

(38) *Caution*! A violent explosion occurred upon concentration of the reaction mixture.

(39) Searle, N. E.; Adams, R. *J. Am. Chem. Soc.* **1993**, *55*, 1649.

2,2′-Dinitrobenzil[37] (21a). Tolane **20a** (19.94 g, 74 mmol) was added to a mixture of potassium permanganate (35.2 g, 222 mmol) dissolved in water (600 mL), Adogen 464, methylene chloride (800 mL), and acetic acid (30 mL). The mixture was stirred and gently refluxed for 5 h, cooled, and decolorized using $NaHSO_3$. The resulting two clear phases were separated, and the yellow organic phase was dried (Na_2SO_4) and filtered through a silica plug. The plug was washed with methylene chloride in such a way that an orange band was kept on the silica. The yellow filtrate was evaporated, and the resulting yellow crystalline solid was washed with methanol to give 18.90 g (85% yield) of benzil **21a**: mp 208–209 °C (lit.[37] 205–206 °C); ^{1}H NMR δ 7.68 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2 H), 7.75–7.79 (m, 2 H), 7.87–7.91 (m, 2 H), 8.28 (dd, J_1 = 8.3 Hz, J_2 = 0.5 Hz, 2 H); IR 1716, 1522, 1341 cm^{-1}; CIMS (NH_3) m/z 318 (M + NH_4, 100), 150 (50).

Diethyl 2,2′-Dinitrobenzil-4,4′-dicarboxylate[28] (21b). Tolane **20b** was oxidized with potassium permanganate as described for the preparation of **21a**. Benzil **21b** was obtained in 84% yield: mp 228–230 °C (lit.[28] 225–227 °C).

5,10-Dihydroindolo[3,2-*b*]indole[27a] (22a). Benzil **21a** (20.54 g, 68 mmol) was reduced with $SnCl_2\cdot H_2O$ as described for the preparation of **22b**.[28] The crude product was boiled with methanol (20 mL), cooled, filtered, and vacuum dried to give 5.08 g (36% yield) of the product: mp >360 °C (lit.[27a] 375 °C); ^{1}H NMR (acetone-d_6) 7.06–7.10 (m, 2 H), 7.16–7.20 (m, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.77 (d, J = 7.8 Hz, 2 H); IR 3402, 1457, 1261, 745 cm^{-1}; EIMS m/z 207 (M + 1, 16), 206 (M, 100), 205 (M – 1, 24), 103 (19).

Diethyl *N,N′*-Dihexyl-5,10-dihydroindolo[3,2-*b*]indole-2,7-dicarboxylate (23b). Crude diethyl 5,10-dihydroindolo[3,2-*b*]indole-2,7-dicarboxylate[28] (**22b**; 4.20 g, 12 mmol) was suspended in dry THF (150 mL). Excess KH (35% in mineral oil) was added followed by hexyl bromide (4.2 mL, 30 mmol). The mixture was stirred and refluxed overnight under an atmosphere of argon, cooled down, and poured into dilute hydrochloric acid. The fluorescent product was taken up with methylene chloride, and the organic phase was dried and filtered through a SiO_2 plug. The filtrate was evaporated, and the crude product was purified on a silica gel column using chloroform as an eluent. The product was recrystallized from a hexane–benzene mixture to yield 3.79 g (61% yield) of yellow-greenish crystals: mp 161 °C; ^{1}H NMR δ 0.84 (t, J = 6.8 Hz, 6 H), 1.22–1.35 (m, 8 H), 1.40-1.52 (m with t at 1.46, J = 7.1 Hz, 10 H), 1.92–2.05 (m, 4 H), 4.45 (q, J = 7.1 Hz, 4 H), 4.54 (t, J = 7.1 Hz, 4 H), 7.83–7.88 (m, 4 H), 8.22 (s, 2 H); ^{13}C NMR δ 13.92, 14.48, 22.46, 26.69, 30.30, 31.50, 45.43, 60.85, 111.98, 116.72, 117.53, 119.38, 124.19, 128.24, 140.51, 167.56; IR 1703, 1489, 1245, 758, 732 cm^{-1}; EIMS m/z 519 (M + 1, 41), 518 (M, 100). Anal. Calcd for $C_{32}H_{42}N_2O_4$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.06; H, 8.19; N, 5.41.

***N,N′*-Dihexyl-5,10-dihydroindolo[3,2-*b*]indole-2,7-dicarbaldehyde (25).** Diester **23b** (1.00 g, 1.93 mmol) was refluxed in 2-propanol (15 mL) containing KOH (1.0 g) for 3 h and cooled down, and the yellow precipitate was filtered off. Vacuum-dried salt was suspended in dry benzene (30 mL), oxalyl chloride (2.5 mL) was added, and the mixture was gently refluxed for 3 h. The solvent was evaporated, the orange residue was vacuum dried, and dry methylene chloride (30 mL) and *N,O*-dimethylhydroxylamine hydrochloride (0.50 g) were added followed by pyridine (1.5 mL). The mixture was stirred at ambient temperature for 4 h, during which a bright-yellow solution was formed. The reaction mixture was filtered through silica gel which was washed with an ethyl acetate–chloroform mixture. The filtrate was evaporated, and the residue was recrystallized from a benzene–hexane mixture and subsequently from ethanol to yield 0.90 g (85% overall yield) of crude yellow 5,10-dihexyl-5,10-dihydro-*N,N′*-dimethoxy-*N,N′*-dimethylindolo[3,2-*b*]-indole-2,7-dicarboxamide: mp 109–111 °C; ^{1}H NMR δ 0.83 (t, J = 7.1 Hz, 6 H), 1.21–1.41 (m, 12 H), 1.93–2.00 (m, 4 H), 3.43 (s, 6 H), 3.62 (s, 6 H), 4.67 (t, J = 7.1 Hz, 4 H), 7.56 (d, J = 8.3 Hz, 2 H), 7.81 (d, J = 8.3 Hz, 2 H), 7.92 (s, 2H); ^{13}C NMR δ 13.68, 22.24, 26.53, 30.08, 31.29, 34.10, 45.16, 60.68, 110.65, 115.29, 116.92, 118.40, 127.11, 127.25, 139.84, 170.55; EIMS m/z 549 (M + 1, 41), 548 (M, 100), 489 (5), 488 (61). Without further purification the amide (0.50 g, 1 mmol) was dissolved in dry THF (25 mL), the solution was cooled down (–78 °C), and DIBAL (3 mL of 1.0 M solution in toluene) was added. The mixture was stirred at low temperature for 4 h, warmed to 0 °C, stirred for 15 min, and poured into ethanol (100 mL) containing concentrated hydrochloric acid (10 mL) which was placed in a refrigerator. Orange crystals were filtered off, washed with hexanes, and dried, and the product was purified on a silica gel column using chloroform as an eluent. The eluate was evaporated, and the product was recrystallized from a hexanes–chloroform mixture to give 0.31 g (80% yield or 68% overall) of orange crystals of dialdehyde **25**: mp 169–176 °C; ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 6 H), 1.25–1.49 (m, 12 H), 1.96–2.02 (m, 4 H), 4.57 (t, J = 7.2 Hz, 4 H), 7.73 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 2 H), 7.96 (d, J = 8.4 Hz, 2 H), 8.04 (s, 2 H), 10.14 (s, 2 H); ^{13}C NMR δ 13.90, 22.46, 26.74, 30.31, 31.48, 45.62, 112.01, 117.65, 118.51, 120.19, 129.19, 131.33, 141.06, 192.18; IR 1678, 1582, 1471, 1231, 1197 cm^{-1}; EIMS m/z 431 (M + 1, 32), 430 (M, 100). Anal. Calcd for $C_{28}H_{34}N_2O_2$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.09; H, 7.97; N, 6.56.

5,5′-Dibromo-2,2′-bithiophene (19). This compound was prepared according to a literature procedure whereby 2,2′-bithiophene was treated with NBS in glacial acetic acid.[26]

2,7-Dibromo-5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole (24). The parent indoloindole **22a** was converted to the *N,N′*-dihexyl compound **23a** as described for **23b** above; the product (0.80 g, 2.1 mmol) was dissolved in pyridine (10 mL), and bromine (5 mL, 1 M in CCl_4) was slowly added at room temperature with stirring. The mixture was stirred for 1 h and poured into dilute hydrochloric acid, and the product was extracted with methylene chloride. The extract was dried and passed through a silica gel plug. The eluate was evaporated, and the solid residue was recrystallized (hexanes) to yield 0.73 g (64% yield) of white solid: mp 160 °C; ^{1}H NMR (CD_2Cl_2) δ 0.83 (t, J = 7.0 Hz, 6 H), 1.21–1.32 (m, 8 H), 1.35–1.43 (m, 4 H), 1.89–1.96 (m, 4 H), 4.42 (t, J = 7.1 Hz, 4 H), 7.25 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 2 H), 7.56 (br s, 2 H), 7.62 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (CD_2Cl_2) δ 14.12, 22.95, 27.15, 30.56, 31.99, 45.97, 113.30, 113.73, 115.73, 119.24, 121.78, 126.41, 141.75; IR 2950, 2926, 2855, 1488, 1256, 1223, 802, 792 cm^{-1}; CIMS m/z 535 (52), 534 (60), 533 (100), 532 (83), 531 (51), 530 (37). Anal. Calcd for $C_{26}H_{32}Br_2N_2$: C, 58.66; H, 6.06; N, 5.26; Br, 30.02. Found: C, 58.69; H, 6.02; N, 5.22; Br, 30.01.

Acknowledgment. This work was supported by the Office of Naval Research, to whom we are grateful. Initial studies were supported by a research grant from the Beckman Institute at Caltech.