Tuning of Ferromagnetic Spin Interactions in Polymeric Aromatic Amines via Modification of Their π-Conjugated System

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Ⓢ Supporting Information

ABSTRACT: Polyarylamine containing *meta*−*para*−*para*-aniline units in the main chain and *meta*−*para*-aniline units in the pendant chains was synthesized. The polymer can be oxidized to radical cations in chemical or electrochemical ways. The presence of *meta*-phenylenes in the polymer chemical structure allows for the ferromagnetic coupling of electronic spins, which leads to the formation of high spin states. Detailed pulsed-EPR study indicates that the $S = 2$ spin state was reached for the best oxidation level. Quantitative magnetization measurements reveal that the doped polymer contains mainly $S = 2$ spin states and a fraction of $S = 3/2$ spin states. The efficiency of the oxidation was determined to be 74%. To the best of our knowledge, this polymer is the first example of a linear doped polyarylamine combining such high spin states with high doping efficiency.
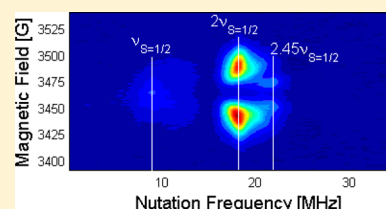
INTRODUCTION

Oligo- and polyanilines have attracted considerable attention due to their interesting properties related to the formation of radical cations stable at room temperature. Moreover, π-conjugated systems of this type of compounds allow for the tuning of their properties by an appropriate modification of molecular structure. For example, polymers containing *para*-phenylene units with extended π-conjugation system exhibit high electrical conductivity, as in the case of classical polyaniline.[1] Polymers and oligomers of this type are also commonly used as efficient hole-transporting materials in OLEDs[2] and in solar cells.[3] The breaking of conjugation by introducing *meta*-phenylene units into the molecular structure leads to the formation of polyanilines with localized radical cations, which makes them promising candidates for magnetic organic materials.

The most developed strategy for building magnetic polymers is based on alternating localized free radicals as "spin-bearing units" and "spin-coupling units" (see strategy A in Scheme 1).[4,5] Spin-coupling units should not only chemically connect spin-bearing units but also promote ferromagnetic interaction between their electronic spins. The most popular spin-coupling units are *meta*-phenylene and its derivatives such as 3,4′-biphenylene and 4,4″-*meta*-terphenylene moieties. This strategy was developed by several groups for different types of spin-bearing units including aniline and arylamine radical cations,[6−13] oligothiophene and oligoacetylene radical cations,[14,15] aromatic nitroxides,[16,17] phenoxyl radicals,[18] biphenyl radical cations,[13] and polyradicals derived from polyarylmethyls.[19−24] The highest spin states (up to $S ≈ 5000$)[22] were obtained for polyradicals derived from polyarylmethyls, but

Scheme 1. Main Strategies for the Design of High-Spin Polymers Reported in the Literature[a]
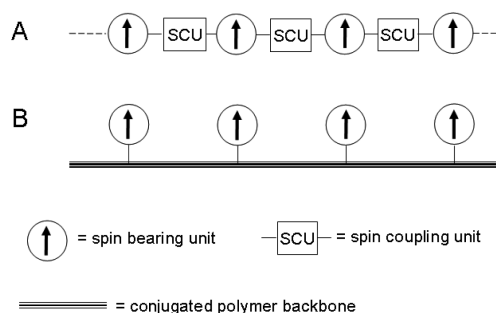
[a]**A**: alternation of spin-bearing units and spin-coupling units. **B**: grafting of spin-bearing units as pendant chains on a conjugated polymer backbone.

these radicals are chemically stable only at low temperature. Today research efforts focus on polyradicals whose free-radical moieties are chemically more stable. This is the case of doped polyarylamines, which have the great advantage that the spin-bearing units, that is, aminium radical cations, can be stable up to room temperature.

The simplest approach to obtain magnetic polyaniline is the synthesis of poly(*meta*-aniline) containing *meta*-phenylene as spin-coupling units and −HN[o+][,8,9] or −PhN[o+][,25] as spin-bearing units. However, in this case, the oxidation of each

amine group is very difficult because of the hole/hole repulsion: no spin state higher than $S = 1$ was ever reported for such polymers, and the radical cations exhibited poor chemical stability.[8,9] It is only in the case of cyclic oligomers of *meta*-aniline such as a cyclophane[26] and a triple-decker,[27] that higher spin states (up to $S = 2$) were achieved very recently.

To decrease the hole/hole repulsion and increase the chemical stability of the radical cation, poly(*meta*−*para*-aniline) and other poly- and oligoarylamines with alternating *para*-phenylene and *meta*-phenylene units were synthetized.[28] It should be noticed that in this case the spin-bearing unit corresponds to a *para*-phenylene diamine radical cation (Wurster's blue type), which is known to be an organic free radical with good stability at room temperature. It has been demonstrated that high-spin states, up to $S = 9/2$ in the case of highly branched polyradicals,[12] can be generated in these compounds after partial oxidation. We have shown that in the case of the simplest linear alternating poly(*meta*−*para*-aniline) most spins are uncoupled ($S = 1/2$) and only a small fraction of them form triplet states.[29] This observation was confirmed in the case of *meta*−*para*-oligomers by Ito et al.,[30] who stated that linear *meta*−*para*-compounds are not adequate to realize high-spin systems. Recently, we have demonstrated that increasing the delocalization within the oligoamine segment used for the spin-bearing unit, as in the case of poly(*meta*−*para*−*para*-aniline), enhances the radical cations stability and results in the formation of pure triplet state ($S = 1$).[31] The concentration of radical cations was estimated to be 65%, which was promising for linear polymers although insufficient to create higher spin states.

The second kind of strategy to realize high-spins systems was to connect free radicals as pendant groups to conjugated polymers or molecules (see strategy B in Scheme 1). Nishide et al. have obtained 3,4′-bis(diphenylamino)stilbene,[32] in which an efficient spin coupling between aminium radical cations was realized by stilbene moiety. Similarly, *para*-phenylenediamine linked as pendant groups to oligo-1,4-phenyleneethynylene and 1,4-phenylenevinylene synthesized by Janssen et al.[33] showed ferromagnetic coupling of radical cations occurring by π-conjugated chains. This strategy was extended to conjugated polymer chains, namely, poly(1,2-phenylenevinylene), poly-(1,4-phenylenevinylene), and poly(phenylacetylene) grafted with aminium radical cations[34−38] or phenoxyl radicals[39−42] and produced high spin states up to $S = 5/2$ for linear chains[37−41] and $S = 5$ for hyperbranched systems.[43]

In this article, we report the synthesis and magnetic properties of a new polyaniline derivative (**PN**) whose structure was designed by applying a combination of both strategies. This polymer consists of a main linear chain with alternation of spin-bearing units and spin-coupling units (according to the strategy A in Scheme 1) and pendant chains with spin-bearing units grafted onto the main chain (according to the strategy B). Considering the promising results (pure $S = 1$ state with a doping efficiency as high as 65%) obtained for the linear poly(*meta*−*para*−*para*-aniline), **PA2**, the designed main chain of **PN** was also composed of *meta*−*para*−*para*-aniline segments. In addition, the grafted pendant chains are introduced, which contain *para*-phenylenediamine spin-bearing units and are linked to the main chain by spin-coupling *meta*-phenylene units (Schemes 1 and 2). The aim of this study is to determine whether the addition of grafted pendant chains with spin-bearing units gives access to higher spin states while maintaining the chemical stability and high doping efficiency
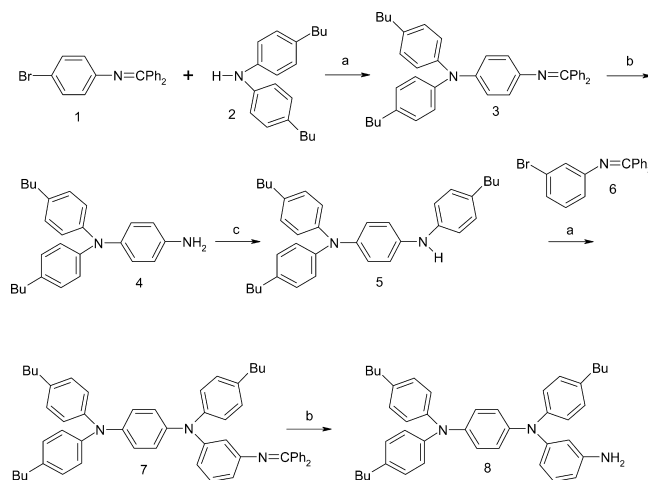
Scheme 2. Chemical Structure of Polymers PA2 and PN
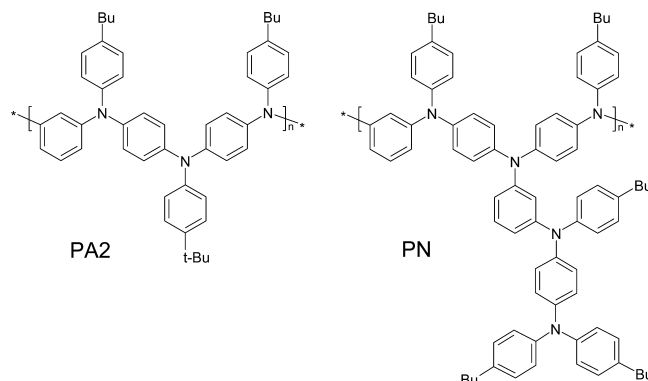
previously obtained for the polymer **PA2**. The doping of **PN** was studied both by chemical and electrochemical oxidations, and the magnetic properties of this polymer have been investigated by pulsed-EPR nutation spectroscopy and SQUID magnetometry.

■ RESULTS AND DISCUSSION

Synthesis. In an attempt to extend the family of high-spin organic materials to enlarged macromolecular system, we have synthesized a new polymer containing aromatic amine units and *meta*-phenylene ferromagnetic coupler in main and pendant chains. The main chain consists of *meta*−*para*−*para*-aniline units and contains three nitrogen atoms in a mer, whereas the pendant chain contains two nitrogen atoms, creating *meta*−*para*-aniline units. To ensure homogeneous distribution of radical cations along the polymer chain, the pendant group was linked to the central nitrogen atom in a mer unit (Scheme 2).

The synthesis of pendant chain was carried out following the procedure shown in Scheme 3 and consisting of protection/deprotection of primary amine groups protocols as well as Hartwig−Buchwald amination reaction. The yield of amination reaction depends strongly on the palladium catalyst used. In the course of the presented synthesis we have used palladium
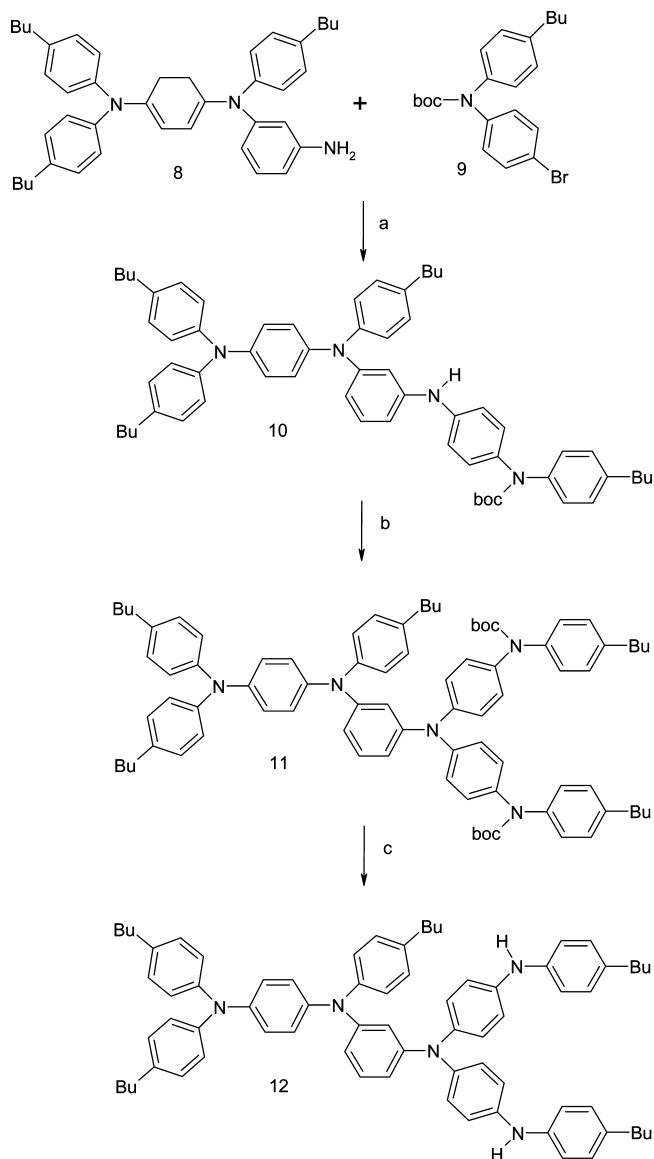
Scheme 3. Synthesis of Pendant Chain[a]

[a](a) Pd(OAc)$_2$, *t*-Bu$_3$P, *t*-BuONa, toluene, 110°C, (b) ammonium formate, Pd/C, MeOH, THF, 65°C, and (c) 1-bromo-4-butylbenzene, Pd(OAc)$_2$, BINAP, *t*-BuONa, toluene, 110°C.

acetate and BINAP or t-Bu$_3$P depending on whether primary or secondary amines were involved in the reaction. Thus, the reaction of compound **1** containing protected primary amine group, that is, *N*-(diphenylmethylene)-4-bromoaniline with di(4-butylphenyl)amine, **2**, in the presence of palladium catalyst gave the compound **3** with a yield of 72%. Primary amine group was deprotected in the presence of ammonium formate and palladium on carbon; then, compound **4** was reacted first with 1-bromo-4-butylbenzene using Pd(OAc)$_2$/BINAP catalyst and then with 3-bromoaniline containing protected amine group, that is, *N*-(diphenylmethylene)-3-bromoaniline, **6**, in the presence of Pd(OAc)$_2$/t-Bu$_3$P to afford compound **7** with 77% yield. The primary amine group was deprotected with 85% yield to give pendant chain compound, **8**.

The monomer was synthesized in a three-step procedure (Scheme 4). In this case, BOC-protected di(4-bromophenyl)-amine, **9** was used to build up the main chain unit of the intended polymer. Compound **8** was reacted with amine **9** in a two-step procedure. We have noticed that the use of two catalytic systems, first Pd(OAc)$_2$/BINAP and then Pd(OAc)$_2$/t-Bu$_3$P, leads to higher yield of 90% and purer compound than a one-step protocol. Finally, monomer (compound **12**) was obtained after deprotection with trifluoroacetic acid with 71% yield. A palladium-catalyzed amination reaction between monomer and 1,3-dibromobenzene afforded polymer **PN** containing *meta*−*para*−*para*-aniline units in the main chain and *meta*−*para*-aniline unit in the pendant chain.

Polymer **PN** exhibited high weight-averaged molecular weight of 495 kDa and the number-averaged molecular weight of 99.3 kDa. The value of M_n was reduced by the formation of oligomers, which were difficult to remove even by consecutive washing with methanol, acetone, hexanes, and diethyl ether.

Electrochemical Studies. The electrochemical properties of **PN** were studied by cyclic voltammetry in dichloromethane with 0.1 M Bu$_4$NBF$_4$ as a supporting electrolyte.

The cyclic voltammogram shows three reversible oxidation waves with a shoulder in the 0 to 0.25 V potential range (Figure 1a). However, the differential pulse measurement (Figure 1b) reveals the presence of five reversible oxidation processes. To understand the possible oxidation reactions in a complex

Scheme 4. Synthesis of Monomer (Compound 12)^a

Figure 1. Cyclic voltammogram (three consecutive scans) obtained for polymer **PN** in CH$_2$Cl$_2$ solution (the concentration of **PN** $c = 10^{-4}$ M) containing an electrolyte 0.1 M Bu$_4$NBF$_4$, (reference electrode − Ag/0.1 M AgNO$_3$ in acetonitrile, scan rate −100 mV/s) (a). Differential pulse voltammogram (b).
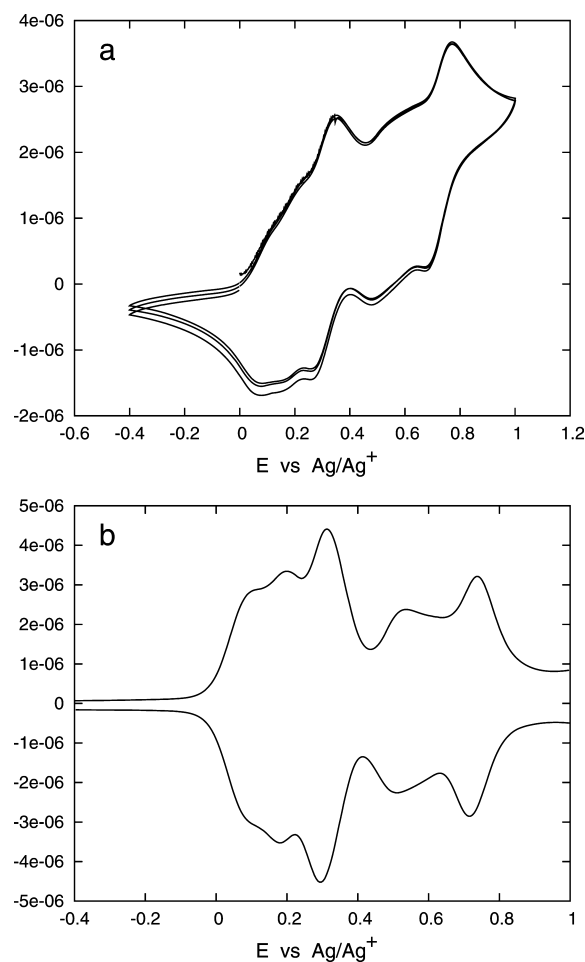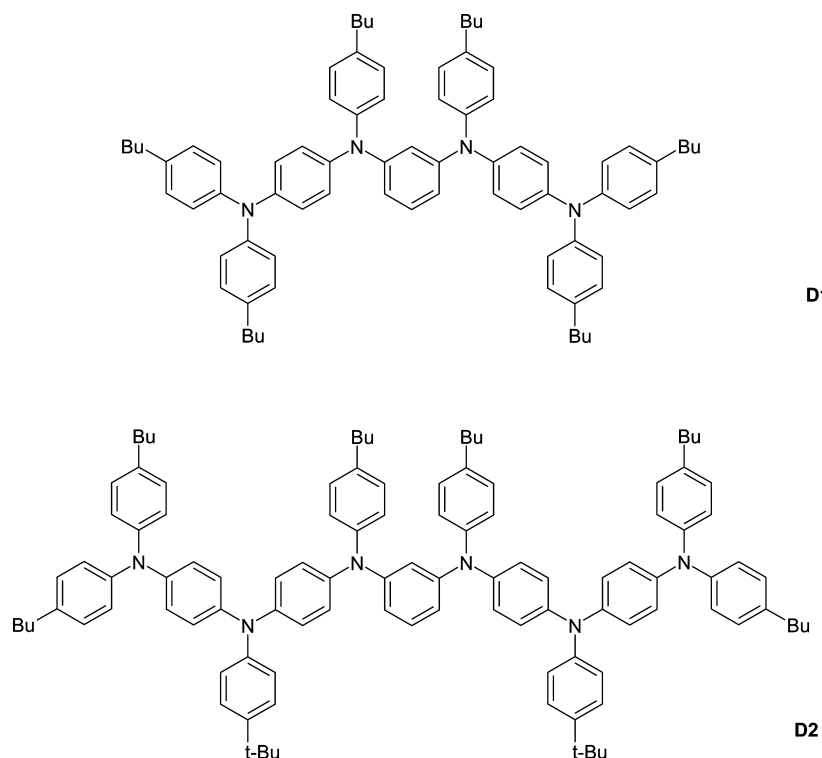
^{a}(a) Pd(OAc)$_2$, BINAP, t-BuONa, toluene, THF, 100°C, (b) Pd(OAc)$_2$, t-Bu$_3$P, t-BuONa, toluene, THF, 100°C, and (c) TFA, toluene.

Scheme 5. Chemical Structures of Dimers D1 and D2

system like **PN**, we have also determined the electrochemical properties of linear polymer **PA2** and dimer **D2** containing *meta−para−para*-aniline units as well as dimer **D1** with *meta−para*-aniline units (see Schemes 2 and 5, Table 1, and the Supporting Information).

Table 1. Oxidation Potentials of Model Compounds D1, D2 and Polymers PA2, PN[a]

compound	E_{1ox} [V]	E_{2ox} [V]	E_{3ox} [V]	E_{4ox} [V]	E_{5ox} [V]
D1	0.14	0.30	0.69	0.76	
D2	0.065	0.15	0.48		
PA2	0.09	0.23	0.50	0.55	
PN	0.10	0.20	0.30	0.53	0.745

[a]Values of the potentials versus Ag/0.1 M AgNO$_3$ in acetonitrile as a reference electrode.

The first oxidation wave in the voltammogram of **PN** appears at 0.1 V (−0.05 V vs Fc/Fc⁺) and is unequivocally due to the removal of one electron from a main chain unit. The first oxidation potential value is in good agreement with that registered for **PA2** and with the value measured by Hirao et al. for linear triarylamine (0.01 vs Fc/Fc⁺).[44]

The second oxidation wave is not well-resolved and appears ca. 0.2 V (0.05 V vs Fc/Fc⁺). Taking into account the values of the first oxidation potential of **D1** and the second oxidation potentials determined for **D2** and **PA2**, we suggest that the second oxidation wave for **PN** is related to two simultaneous processes:

(i) the removal of one electron from a main chain *meta−para−para*-aniline unit neighboring another such unit, which already bears a radical cation

(ii) the oxidation of a pendant chain *meta−para*-aniline unit which has no radical cation in its close vicinity

The contribution of the process (i) in the second oxidation wave is supported by the results obtained to date for linear oligo(*meta−para*-anilines).[28b,30] The electrochemical studies reported by Wienk et al.[28b] and Ito et al.[30] for hexaanilines containing three *para*-phenylenediamine units connected via two *meta*-phenylenes showed that the oxidation potential of central diamine unit is higher than that of peripheral ones as a result of charges in two adjacent units. These studies established also that in oligoarylamines where two neighboring *para*-phenylenediamine units are connected via a *meta*-phenylene the difference between the first and second oxidation potential ($E_2 − E_1 \approx 0.15$ V) is smaller than the one observed in oligoarylamines, where these units are connected via *para*-phenylene ($E_2 − E_1 \approx 0.25$ V), due to the nonresonant nature of the *meta*-phenylene. The process (ii) is also possible considering the value of the first oxidation potential of **D1** and other similar compounds.[28a,b,30]

The third oxidation wave at 0.3 V (0.15 V vs Fc/Fc⁺) corresponds to the removal of one electron from a pendant chain unit, which has a radical cation in its vicinity. This value is similar to that reported for the formation of radical cation in *para*-phenylenediamine moiety[28b] and to the second oxidation wave of **D1**. The two consecutive oxidation waves of **PN** at 0.53 (0.38 V vs Fc/Fc⁺) and 0.745 V (0.595 V vs Fc/Fc⁺) can be attributed to the removal of a second electron from a *meta−para−para*-aniline unit of the main chain and a second electron from a *meta−para*-aniline of the pendant chain, respectively. E_{ox4} value agrees with that reported for **PA2** and **D2** and for the corresponding oxidation of triamine (0.36 V vs Fc/Fc⁺) and nonamine (0.38 V vs Fc/Fc⁺),[44] whereas E_{ox5} value is lower than that reported for tetraamine (0.66 V vs Fc/Fc⁺)[28b] and higher than the value determined for **D1** for the third oxidation process. These observations illustrate the influence of hole/hole electrostatic repulsion on amine oxidation potentials, even in the presence of a *meta*-phenylene.

UV−vis Studies. The formation of radical cations in polyaniline can be generated using chemical oxidation as well. The oxidation process of **PN** was studied using UV−vis-NIR spectroscopy. The polymer was oxidized with *tris*(4-bromophenyl)amminium hexachloroantimonate, TBA·SbCl$_6$, in CH$_2$Cl$_2$/BuCN solution. The UV−vis spectrum of neutral polymer **PN** in CH$_2$Cl$_2$ shows one band at 322 nm ($\varepsilon = 9.4 \times 10^4$ M^{-1} cm^{-1}), which can be attributed to the $\pi-\pi^*$ transition in phenylene rings (Figure 2a). The same $\pi-\pi^*$ band position
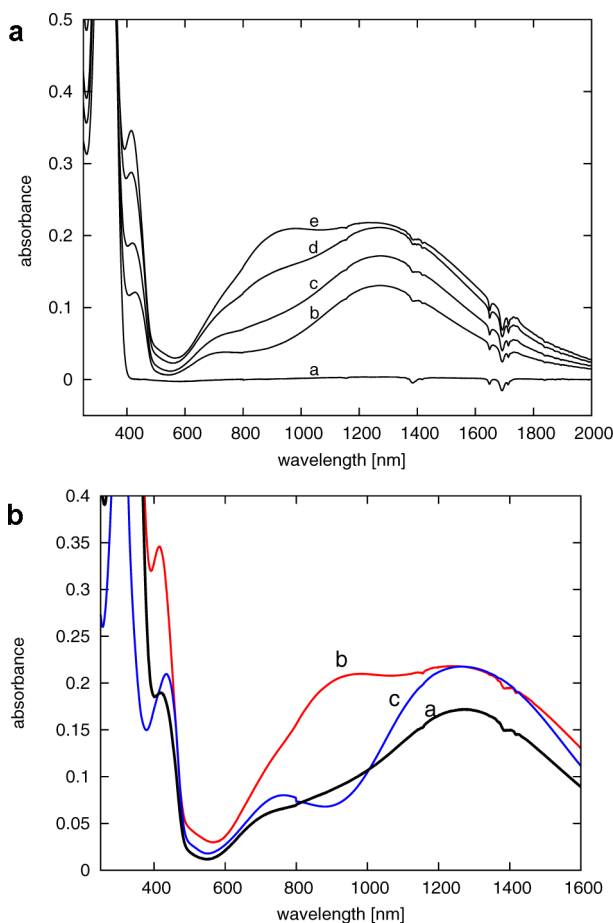
Figure 2. (a) UV−vis-NIR spectra of polymer **PN** oxidized with TBA·SbCl$_6$ in CH$_2$Cl$_2$/BuCN solution (the concentration of PN $c = 10^{-4}$ M); the Ox/PN1 molar ratio: (a) 0, (b) 0.5, (c) 1, (d) 1.5, and (e) 2. (b) UV−vis-NIR spectra of polymer **PN** and **PA2** oxidized with TBA·SbCl$_6$ in CH$_2$Cl$_2$/BuCN solution (the concentration of PN or PA2 $c = 10^{-4}$ M): (a) Ox/PN = 1, (b) Ox/PN = 2, and (c) Ox/PA2 = 1.

was observed in the case of polyaniline containing *meta−para−para*-aniline units without pendant chains (**PA2**).[45] Upon oxidation, three new bands characteristic of radical cations appear. These bands are located at 427, ca. 730, and 1270 nm. The presence of two bands in the vis-NIR region is similar to that observed for triarylamine or nonamine studied by Hirao et al.[44] The location of these bands is also similar to that registered for poly(*meta−para−para*-aniline), **PA2**.[45] Thus, it leads to the conclusion that at the beginning the oxidation of **PN** generates radical cations in the main chain. This observation is in agreement with electrochemical measurements that indicate that two first oxidation waves are mainly related to the oxidation of two neighboring main chain units. However,

the close inspection of the spectra of **PN** and **PA2** oxidized to one radical cation per mer shows significant differences (Figure 2b). In the case of Ox/PN = 1 spectrum (in the following, Ox/PN = x stands for "x equivalents of oxidant per one equivalent of PN mer"), one can observe the decrease in the intensity of the band at 1270 nm as compared with that in the spectrum of Ox/PA2 = 1, which indicates that the concentration of radical cations in the main chain is lower for **PN** than for **PA2**. Moreover, the Ox/PN = 1 spectrum reveals an absorption ca. 900 nm, which can be attributed to the presence of radical cations located on the pendant chain. Further oxidation causes the increase in the intensities of the bands typical for radical cations of the main as well as pendant chains (the spectrum of Ox/PN = 1.5, Figure 2a). At this oxidation level the concentration of radical cations in the main chain reaches its maximum. The character of UV−vis-NIR spectra changes is in agreement with electrochemical studies, showing simultaneous oxidation of the main and pendant chains in an intermediate oxidation potential range. Then, the spectrum of Ox/PN = 2 shows the appearance of a band at 910 nm associated with the formation of radical cations in the pendant chain. The position of the last band is similar to that observed in the case of oxidized poly(*meta−para*-aniline).[45] This result is in accordance with the appearance of the third oxidation wave in cyclic voltammogram associated with the oxidation of pendant chain.

Pulsed-EPR Nutation and SQUID Magnetometry. Pulsed-EPR nutation spectroscopy enables one to discriminate and identify the electronic spin states present in a complex sample. For this reason, it is well-adapted to the study of polyradicals obtained by doping of oligomers[26,28d,30,46−50] and polymers.[29,31] The corresponding spectra can be rationalized by using eq 1 (see Experimental Section), which provides a simple relationship between the observed nutation frequency and the quantum numbers S and m_S of a given spin state.

The successive oxidation states obtained by chemical oxidation of the polymer **PN** by TBA·SbCl$_6$ in CHCl$_3$/AcCN solutions were studied by pulsed-EPR nutation spectroscopy (Figure 3). In the spectrum recorded for Ox/PN = 1 molar ratio, one can see three main signals (Figure 3, lower frame). The most intense signal is observed at $\nu_{nut} = \nu_{S=1/2} = 23.5$ MHz and corresponds to a S = 1/2 spin state. The second, much less intense, is observed at 32 MHz, which is close to the nutation frequency expected for a S = 1 state (following eq 1 $\nu_{nut(S=1)} = \sqrt{2} \cdot \nu_{S=1/2} = 33$ MHz). A third weaker signal is observed at 39 MHz close to the expected nutation frequency for the |3/2,+3/2⟩ ↔ |3/2,+1/2⟩ and |3/2,−3/2⟩ ↔ |3/2,−1/2⟩ transitions of a S = 3/2 state ($\nu_{nut} = \sqrt{3} \cdot \nu_{S=1/2} = 41$ MHz). Thus at this oxidation level, most electronic spins are uncoupled, and only few of them are coupled by two or three to yield S = 1 and 3/2 states.
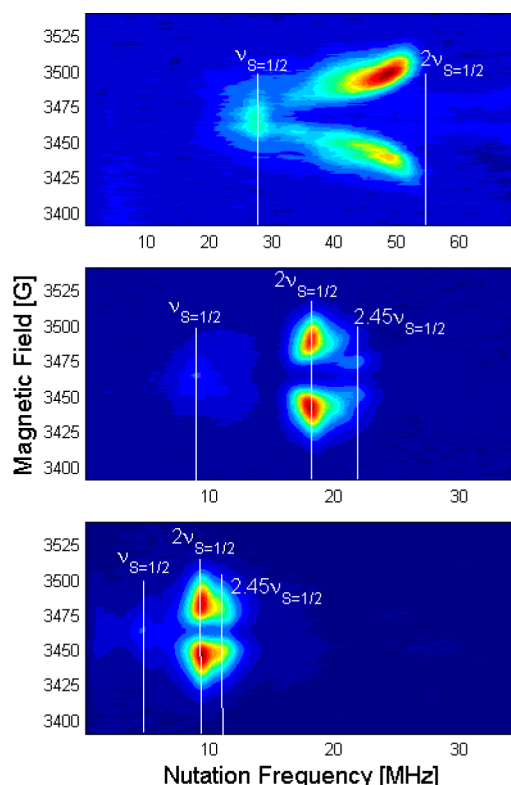
When the sample is further doped up to Ox/PN = 2 molar ratio, the spectrum changes drastically (Figure 3, middle frame). The most intense signals are observed at a higher nutation frequency ∼44 MHz that is intermediate between the nutation frequency expected for the |3/2,+3/2⟩ ↔ |3/2,+1/2⟩ and |3/2,−3/2⟩ ↔ |3/2,−1/2⟩ transitions of S = 3/2 spin states ($\nu_{nut} = \sqrt{3} \cdot \nu_{S=1/2} = 41$ MHz) and the nutation frequency ($\nu_{nut} = 2 \cdot \nu_{S=1/2} = 47$ MHz) that is expected either for the |3/2,+1/2⟩ ↔ |3/2,−1/2⟩ transitions of S = 3/2 states or for the |2,+2⟩ ↔ |2,+1⟩ and |2,−2⟩ ↔ |2,−1⟩ transitions of S = 2 spin states. From this spectrum, one can conclude that at this oxidation level most electronic spins are coupled by three or by four and yield S = 3/2 or 2 spin states. Further doping up to Ox/PN = 3
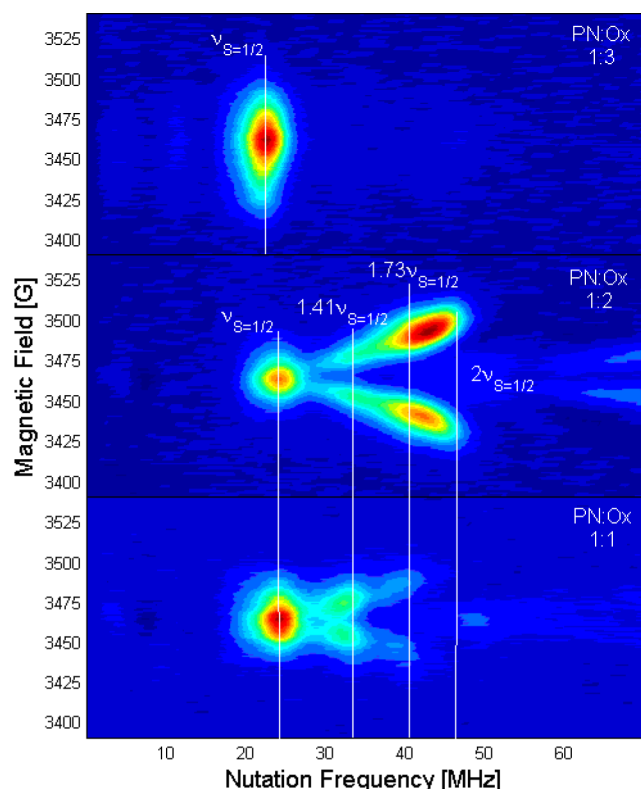
Figure 3. Monitoring of the chemical oxidation of the polymer **PN** by 2D pulsed-EPR nutation. The polymer **PN** was oxidized with TBA·SbCl$_6$ in CHCl$_3$/AcCN solution (the concentration of PN c = 7.5 × 10^{-3} M) with the following molar ratios: Ox/PN = 1 (lower frame), 2 (middle frame), and 3 (upper frame).

Figure 4. Pulsed-EPR nutation study of a sample of polymer **PN** oxidized with the molar ratio: Ox/PN = 2. Experiments were performed at various microwave power values: B_1 = 4.5 MHz (lower frame), 8.9 MHz (middle frame) and 26.8 MHz (upper frame). **PN** was oxidized with TBA·SbCl$_6$ in CHCl$_3$/AcCN (1/1 v/v) solution (the concentration of PN c = 7.5 × 10^{-3} M).

molar ratio (Figure 3, upper frame) yielded a pulsed-EPR nutation spectrum with only one nutation frequency (22 MHz) corresponding to S = 1/2 spin state and indicating that no more high spin states are present for this oxidation level.

Another set of experiments corresponding to the sample oxidized with Ox/PN = 2 molar ratio was performed to identify and quantify the involved high spin state(s). Pulsed EPR-nutation spectra reported in Figure 4 were recorded using different values of microwave power, which correspond to different values of the nutation frequency for S = 1/2 state, $\nu_{S=1/2}$. In the spectrum recorded at high power (see Figure 4, upper frame $\nu_{S=1/2}$ = 26.8 MHz), the most intense signal is obtained at 49 MHz nutation frequency, which does not correspond to the frequencies expected for transitions in S = 3/2 or 2 spin states ($\sqrt{3}\cdot\nu_{S=1/2}$ = 46 MHz, $2\cdot\nu_{S=1/2}$ = 54 MHz, and $\sqrt{6}\cdot\nu_{S=1/2}$ = 66 MHz). Such intermediate values can be observed when high microwave power is used because eq 1 is valid only when $B_1 \ll D$. (D stands for the zero-field splitting parameter of the studied high spin state species, and B_1 stands for the amplitude of the magnetic field component of the microwave EPR pulse.) To check this hypothesis, lower microwave power levels were used corresponding to $\nu_{S=1/2}$ = 8.9 MHz and $\nu_{S=1/2}$ = 4.5 MHz (in Figure 4 middle and lower frames), respectively. In these two experiments, one can see that the most intense signals are observed at nutation frequencies corresponding exactly to $2\cdot\nu_{S=1/2}$ and that some smaller signals are observed at $\sqrt{6}\cdot\nu_{S=1/2}$. The observation of main signals at $2\cdot\nu_{S=1/2}$ and $\sqrt{6}\cdot\nu_{S=1/2}$ nutation frequencies is diagnostic of S = 2 spin state because all spin transitions of S = 2 states are accounted for by these nutation frequencies.

Moreover, the absence of signal at $\sqrt{3}\cdot\nu_{S=1/2}$ suggests the absence of S = 3/2 spin state. Thus, from pulsed-EPR nutation experiments, one could conclude that at Ox/PN = 2 molar ratio the oxidized **PN** polymer yields a pure S = 2 spin state.

The same sample prepared at Ox/PN = 2 molar ratio was also studied by SQUID magnetometry. Magnetization measurements versus magnetic field at 2K are shown in Figure 5. These measurements are corrected from diamagnetic contributions as described in the Experimental Section. The experimental M = $f(H)$ curve does not fit with the theoretical Brillouin function expected for a system containing only S = 2 spin states. Magnetization saturates slower when the magnetic field increases than expected from the theoretical Brillouin function for a S = 2 spin state. On the opposite, the experimental M = $f(H)$ curve saturates quicker than expected from the theoretical Brillouin function for S = 3/2 spin states (Figure 5, upper frame).

A possible way to rationalize these results would be that the sample under study contains both S = 2 and 3/2 spin states. The lower frame of Figure 5 shows the best numerical fitting of the experimental data by a weighted sum of S = 3/2 and 2 Brillouin functions. This numerical fitting corresponds to a mix of 34.5% of S = 3/2 spin states (4.3 × 10^{-8} moles) and 65.5% of S = 2 spin states (8.1 × 10^{-8} moles). The quantity of **PN** mers in the sample is 3.36 × 10^{-7} moles. If one considers that two mers oxidized at the molar ratio Ox/PN = 2 are necessary to obtain four radical cations ferromagnetically coupled in a S = 2 spin state, the yield in quintet spin state is 48%. With the same assumption, the yield in S = 3/2 spin state is 26%.
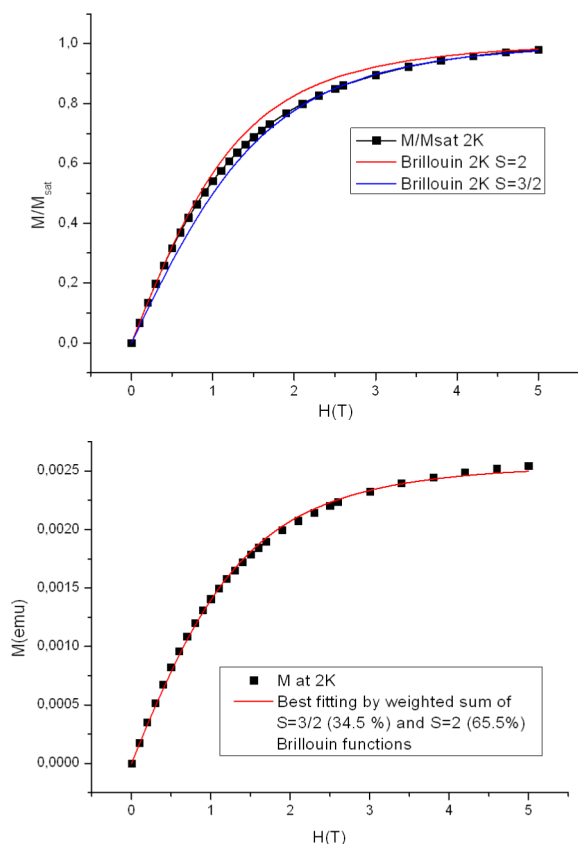
Figure 5. SQUID magnetometry study of a sample of polymer **PN** oxidized with the molar ratio: Ox/PN = 2. Upper frame: $M = f(H)$ curve recorded at T = 2K, normalized, corrected for diamagnetism and compared with normalized Brillouin functions for S = 2 and 3/2. Lower frame: $M = f(H)$ curve recorded at T = 2 K, corrected for diamagnetism, and compared with the best fit obtained by linear combination of S = 2 and S = 3/2 Brillouin functions. Fitting results %(S = 3/2) = 34.5, %(S = 2) = 65.5, R = 0.9987. PN was oxidized with TBA·SbCl$_6$ in CHCl$_3$/AcCN (1/1 v/v) solution (the concentration of PN c = 7.5 × 10^{-3} M), and the same solution was used to prepare sample studied by pulsed-EPR, as reported in Figure 4.

Therefore, the overall doping efficiency of the polymer **PN** in these experiments can be estimated to 74%.

The slight discrepancy between the results obtained by pulsed EPR nutation experiments (pure S = 2 spin state) and SQUID magnetometry (the behavior corresponding to a mix of S = 2 and 3/2) for samples prepared from the same solution of doped **PN** is most probably due to the fact that radical cations on *meta–para*-aniline units of pendant chains are less chemically stable than radical cations on *meta–para–para*-aniline units of the main chain[28d,29,45,46,50,52] and that the times for sample preparation and introduction are longer for SQUID experiments than for EPR experiments. However, pulsed-EPR and SQUID measurements clearly demonstrate that S = 2 is the main spin state present in samples doped up to Ox/PN = 2 molar ratio and that **PN** can be doped with high efficiency.

The observed high-spin states $S \geq 3/2$ compare well with those of polymers bearing arylamines connected as pendant chains to a conjugated linear polymer (strategy B, see Scheme 1) because in these last systems the highest spin states obtained range between S = 3/2 and 5/2.[34–38] The doping efficiency of 74% obtained for **PN** is comparable to the highest 70–80% doping efficiencies reported for doped polyarylamines in the literature.[6,11–13,51] Several other doped polyarylamines with high-spin states[13,53] (up to S = 9/2)[12] were reported, but it was in the case of branched polyarylamines. To the best of our knowledge, the polymer **PN** is the first example of a $S \geq 3/2$ high-spin state doped polyarylamine with a linear main chain constituted of alternating spin-bearing units (arylamines) and spin-coupling units. This improves significantly the results we reported previously with the linear polymer **PA2** having the same linear chain with *meta–para–para*-aniline units.[31] It further validates our strategy of grafting small pendant chains as additional spin-bearing units to reach higher spin states.

The most surprising feature of **PN** doped with 2:1 oxidant:mer stoichiometry is that according to pulsed EPR nutation spectroscopy most of the electronic spins are coupled in $S \geq 3/2$ states but with very few uncoupled S = 1/2 electronic spins and without any spin state higher than S = 2. A similar behavior was observed for **PA2**, which exhibited pure S = 1 state with 65% doping efficiency.[31] In both cases, the reasons for such rather limited high-spin states are not yet firmly established.

The first possible cause for the formation of spin states not higher than S = 2 in doped **PN** is incomplete doping. The number of radical cations involved in the S = 3/2 and 2 spin states measured by SQUID magnetometry corresponds to 74% of doped *meta–para–para* units (main chain) and *meta–para*-aniline units (pendant chains). It is far from 100% and can imply that a high fraction of the *meta–para–para*-aniline units of the main chain remain undoped preventing the coupling of a large number of spins along the polymer chain. The second reason that can be invoked is unfavorable local conformations in some units of the polymer chain. The variation of the local conformation can change the nature of the magnetic interaction from ferromagnetic to antiferromagnetic ones, even if strongly ferromagnetic coupling units such as *meta*-phenylenes are involved.[54] The third possible reason is the actual delocalization of the spin density in the polymer chain. In the main chain, a given electronic spin could be delocalized to only a part of the *meta–para–para*-aniline unit and would not be able to interact with both neighboring units in the main chain. Such an explanation seems to be in contradiction with the electronic density of magnetic orbitals in *meta–para–para*-aniline units computed by DFT calculations for some dimers including two *meta–para–para*-aniline units (**D2**) in our previous report because this computed electronic density was well spread over the whole unit.[31] However, these previously reported calculations were performed for the diradical cations of **D2** without taking the solvent and the counterions into account. Calculations including counterions and a dielectric medium are underway, and preliminary results indicate that counterions have a strong influence on the delocalization of the spin density. Moreover, for oligoanilines containing only *para*-substituted phenyl, it has been reported that electronic spin corresponding to one radical cation is less delocalized than expected and is confined essentially to one phenylenediamine unit.[55] Similar confinement can be also considered in the case of the polymer studied. Further EPR, SQUID, and DFT calculations studies on model compounds are underway in our laboratories to investigate what is the actual delocalization of electronic spins in the *meta–para–para*-aniline units of such systems and what is the effect of local conformations on the coupling of electronic spins in such systems.

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■ CONCLUSIONS

In summary, the oxidation of **PN** polymer leads to the creation of spins states with high multiplicity up to $S = 2$. The efficiency of the oxidation of **PN** to radical cations was determined to be at least 74%. We currently investigate the hypotheses that (i) incomplete doping, (ii) antiferromagnetic coupling due to local conformation of the main chain, and (iii) the lack of delocalization of electronic spins in *meta−para−para*-aniline units could impede the ferromagnetic coupling of a larger number of spins throughout the polymer chain.

■ EXPERIMENTAL SECTION

Characterization Techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury (400 and 100 MHz) spectrometer and referenced with respect to TMS and solvents. IR spectra were monitored on Bio-RAD FTS-165 spectrometer using KBr pellets. UV−vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Mass spectra were measured by EI method on an AMD 604 mass spectrometer. All synthesized compounds studied were subject to C, H, N, and Br elemental combustion analysis.

Reagents. 4-Butylaniline, 4-bromoaniline, 3-bromoaniline, 1-bromo-4-butylbenzene, 1,3-dibromobenzene, 1,4-dibromobenzene, benzophenone, palladium acetate (Pd(OAc)$_2$), palladium on carbon (10%), tris-*tert*-butylphosphine (*t*-Bu$_3$P), 2,2′-bis(diphenylphosphino)-1,1′-binaphtyl (BINAP), sodium *tert*-butoxide (*t*-BuONa), di-*tert*-butyl dicarbonate (BOC), 4-(dimethylamino)pyridine (DMAP), trifluoroacetic acid (TFA), molecular sieves (5 Å), ammonium formate, anhydrous toluene, and anhydrous acetonitrile were purchased from Aldrich. 4-Butylaniline was distilled under reduced pressure.

All glassware was oven-dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.

General Procedure for C−N Bonding Formation. Palladium acetate (3%$_{mol}$) and phosphine (9%$_{mol}$) were mixed in 5 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then, aryl bromide (1 mmol), amine (1 mmol), sodium *tert*-butoxide (1.5 mmol), and ca. 10 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. After the mixture was cooled to room temperature, 50 mL of distilled water was added and the organic layer separated. The aqueous phase was extracted with three 10 mL portions of diethyl ether. The combined organic phases were dried over MgSO$_4$.

N-(Diphenylmethylene)-4-bromoaniline, 1. The compound was prepared according to the method described by Sadighi et al.[56] The crude product was recrystallized from ethyl acetate/MeOH to give yellow crystals (82.4% yield). M$_p$: 82−83 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.73 (dd, J = 8.0, 0.8 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.32−7.24 (m, 5H), 7.11 (dd, J = 7.6, 1.2 Hz, 2H), 6.60 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 168.9, 150.2, 139.3, 135.8, 131.5, 131.0, 129.3, 128.8, 128.2, 128.1, 122.7, 116.2. IR (cm^{-1}): 3054, 3026, 1612, 1595, 1580, 1478, 1296, 1222, 827, 702, 690. Anal. Calcd for C$_{19}$H$_{14}$BrN: C, 67.88; H, 4.17; N, 4.17; Br, 23.78. Found: C, 67.41; H, 4.24; N, 4.26; Br, 23.65.

Di(4-butylphenyl)amine, 2. 4-Butylaniline, 2.98 g (20 mmol), 1-bromo-4-butylbenzene, 4.69 g (22 mmol), sodium *tert*-butoxide, 2.88 g (30 mmol), palladium acetate, 134.7 mg (0.6 mmol), and BINAP, 1.12 g (1.8 mmol) were dissolved in 40 mL of dry toluene under an argon atmosphere. The reaction

mixture was stirred and heated to 110 °C for 20 h. Removal of the solvents followed by chromatography on silica gel (CH$_2$Cl$_2$/hexanes 1:2, containing 1%$_{vol}$ of Et$_3$N) resulted in pale-yellow oil, 5.15 g (18.3 mmol, 91.6% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.01−7.00 (m, 4H), 6.91−6.88 (m, 4H), 4.98 (s, 1H), 2.48 (t, J = 7.6 Hz, 4H), 1.56−1.48 (m, 4H), 1.33−1.23 (m, 4H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ, 141.9, 135.2, 129.5, 118.2, 35.3, 34.2, 22.6, 14.1. IR (cm^{-1}): 3397, 3025, 2957, 2928, 2856, 1610, 1516, 1458, 1310, 823. Anal. Calcd for C$_{20}$H$_{27}$N; C, 85.41; H, 9.61; N, 4.98. Found: C, 85.01; H, 9.37; N, 5.60.

N-(Diphenylmethylene)-N′,N′-di(4-butylphenyl)-1,4-phenylenediamine, 3. Palladium acetate, 95.6 mg (0.426 mmol) and tri*tert*-butylphosphine, 258.5 mg (1.278 mmol) were dissolved in 2 mL of dry toluene under an argon atmosphere and stirred at room temperature for 15 min. Then, compound **1**, 4.77 g (14.2 mmol), compound **2**, 3.99 g (14.2 mmol), sodium *tert*-butoxide, 1.92 g (20 mmol), and ca. 40 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110 °C for 20 h. Removal of the solvents, followed by crystallization from ethyl acetate, afforded titled compound **3** as pale-yellow crystals (5.51 g, 10.3 mmol, 72% yield). M$_p$. 108.3−110.1 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.74 (dd, J = 6.8, 1.6 Hz, 2H), 7.46 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 6.0 Hz, 2H), 7.32−7.30 (m, 3H), 7.17−7.14 (m, 2H), 7.00 (d, J = 8.4 Hz, 4H), 6.90 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.8 Hz, 4H), 2.54 (t, J = 7.8 Hz, 4H), 1.60−1.54 (m, 4H), 1.41−1.32 (m, 4H), 0.93 (t, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 145.9, 145.6, 143.8, 139.9, 136.8, 136.6, 130.5, 129.6, 129.2, 128.9, 128.5, 128.1, 127.9, 124.1, 123.5, 122.4, 35.0, 33.7, 22.4, 14.0. IR (cm^{-1}): 3026, 2955, 2928, 2857, 1601, 1570, 1506, 1496, 1318, 1283, 834, 695. Anal. Calcd for C$_{39}$H$_{40}$N$_2$: C, 87.31; H, 7.46; N, 5.23. Found: C, 86.98; H, 7.46; N, 5.26.

N,N-Di(4-butylphenyl)-1,4-phenylenediamine, 4. The compound **3**, 7.35 g (13.7 mmol), ammonium formate, 12.95 g (205.4 mmol), and palladium on carbon, 10%, 1.45 g (1.37 mmol) were added to the reaction flask and purged with argon. Methanol (60 mL) and THF (30 mL) were added. The resulting mixture was stirred and heated to 65 °C for 4 h. The reaction mixture was cooled to room temperature and concentrated. The residue was taken up in dichloromethane and filtered through Celite. The solvent was evaporated and the crude product was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/hexanes (2:1) to give a bright brown oil, 4.83 g (12.9 mmol, 94% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.00 (d, J = 8.4 Hz, 4H), 6.96−6.92 (m, 6H), 6.63 (d, J = 8.4 Hz, 2H), 3.56 (s, 2H), 2.54 (t, J = 7.8 Hz, 4H), 1.62−1.54 (m, 4H), 1.44−1.32 (m, 4H), 0.94 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 146.1, 142.5, 139.5, 135.9, 128.8, 127.3, 122.4, 116.1, 34.9, 33.7, 22.4, 14.0. IR (cm^{-1}): 3375, 3026, 2957, 2928, 2856, 1606, 1507, 1324, 1267, 828. Anal. Calcd for C$_{26}$H$_{32}$N$_2$: C, 83.87; H, 8.60; N, 7.53; Br. Found: C, 83.52; H, 8.90; N, 7.64.

N-(4-Butylphenyl)-N′,N′-di(4-butylphenyl)1,4-phenylenediamine, 5. The same procedure as for compound **2** was followed using 4.78 g (12.8 mmol) of diamine **4**, 3 g (14.08 mmol) of 1-bromo-4-butylbenzene, 1.84 g (19.2 mmol) of sodium *tert*-butoxide, 86.2 mg (0.384 mmol) of Pd(OAc)$_2$, and 0.72 g (1.152 mmol) of BINAP in 30 mL of dry toluene. The resulting material was chromatographed on silica gel eluting with CH$_2$Cl$_2$/hexanes (1:3) to give an oil, 5.18 g (10.3 mmol, 80.5% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.21 (d, J = 8.4 Hz,

4H), 7.10 (d, J = 8.4 Hz, 2H), 7.00−6.95 (m, 6H), 6.86 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 9.2 Hz, 2H), 4.94 (s, 1H), 2.52−2.42 (m, 6H), 1.54−1.45 (m, 6H), 1.31−1.21 (m, 6H), 0.89−0.82 (m, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 145.9, 141.5, 141.2, 138.9, 136.4, 135.3, 129.2, 129.0, 126.0, 123.0, 118.8, 117.7, 35.0, 34.9, 33.8, 33.7, 22.4, 22.3, 14.0. IR (cm^{-1}): 3394, 3026, 2956, 2928, 2856, 1608, 1506, 1465, 1309, 1276, 825. Anal. Calcd for C$_{36}$H$_{44}$N$_2$: C, 85.71; H, 8.73; N, 5.56. Found: C, 85.61; H, 9.07; N, 5.60. M$^+$/z = 504.5.

N-(Diphenylmethylene)-3-bromoaniline, **6**. This compound was prepared following the same procedure as in the case of **1**. The crude product was recrystallized from ethyl acetate/MeOH to give yellow crystals (77% yield). M_p: 68.5−69.3 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.74 (dd, J = 7.2, 1.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 7.31−7.27 (m, 3H), 7.12−7.10 (m, 2H), 7.05−7.03 (m, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.92 (t, J = 2.0 Hz, 1H), 6.61 (dd, J = 8.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 169.2, 152.6, 139.2, 135.6, 131.0, 129.8, 129.4, 128.9, 128.2, 128.0, 126.0, 124.0, 122.1, 119.5. IR (cm^{-1}): 3027, 1615, 1586, 1562, 1466, 1294, 960, 856, 778, 692. Anal. Calcd for C$_{19}$H$_{14}$BrN: C, 67.88; H, 4.17; N, 4.17; Br, 23.78. Found: C, 67.35; H, 4.30; N, 4.22; Br, 23.38.

Compound, **8**. The same procedure as that for compound **3** was followed using 4.34 g (8.6 mmol) of compound **5**, 2.79 g (8.6 mmol) of compound **6**, 1.16 g (12 mmol) of sodium *tert*-butoxide, 57.7 mg (0.26 mmol) of Pd(OAc)$_2$, and 155.1 mg (0.77 mmol) of *t*-Bu$_3$P in 40 mL of dry toluene. The crude product was reduced according to the procedure described for compound **4**. The product was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/hexanes (2:1 with 1% v/v of Et$_3$N) to give 4.34 g of a pale-brown oil (7.3 mmol, 85% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.21−7.18 (m, 6H), 7.08 (d, J = 2 Hz, 4H), 6.96−6.92 (m, 7H), 6.66 (dd, J = 8, 2 Hz, 1H), 6.39 (t, J = 2.2 Hz, 1H), 6.00 (dd, J = 7.6, 2.4 Hz, 1H), 2.63 (s, 2H), 2.42 (t, J = 7.7 Hz, 6H), 1.51−1.45 (m, 6H), 1.29−1.19 (m, 6H), 0.86−0.81 (m, 9H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ, 149.7, 148.2, 146.4, 146.3, 145.5, 144.4, 137.2, 137.1, 130.1, 129.6, 129.5, 125.7, 125.0, 124.9, 124.4, 113.9, 110.2, 109.3, 35.4, 35.3, 34.1, 34.0, 22.7, 14.1. IR (cm^{-1}): 3375, 3026, 2956, 2927, 2856, 1603, 1503, 1464, 1316, 1270, 829. Anal. Calcd for C$_{42}$H$_{49}$N$_3$: C, 84.71; H, 8.23; N, 7.06. Found: C, 84.42; H, 8.58; N, 7.00. M$^+$/z = 595.6.

(4-Butylphenyl)-(4′-bromophenyl)-N-(tert-butoxycarbonyl)amine, **9**. Palladium acetate, 202 mg (0.9 mmol), and BINAP, 1.68 g (2.7 mmol) were mixed in 5 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then, 1,4-dibromobenzene, 7.08 g (30 mmol), 4-butylaniline, 4.47 g (30 mmol), sodium *tert*-butoxide, 4.05 g (42 mmol), and ca. 55 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated to 110 °C for 20 h. After the evaporation of solvents, the crude product was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/hexanes (1:1 v/v) and then recrystallized in ethyl acetate/methanol to give 8.87 g (29.2 mmol, 97.3% yield) of (4-butylphenyl)-(4′-bromophenyl)amine. The resulting product was mixed with 4-(dimethylamino)pyridine, 0.73 g (5.8 mmol, 20%$_{mol.}$), and di-*tert*-butyl dicarbonate, 9.52 g (43.68 mmol) in 45 mL of dry THF. The mixture was heated to reflux for 3 h. After evaporation of the solvents the product was purified by chromatography eluting with CH$_2$Cl$_2$/hexanes (1:1 v/v) to give a slightly yellow resin, 10.02 g (24.8 mmol, 85% yield). M_p 38.3−40.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ, 7.41−7.38 (m,

2H), 7.13−7.06 (m, 6H), 2.58 (t, J = 7.6 Hz, 2H), 1.58−1.54 (m, 2H), 1.44 (s, 9H), 1.38−1.31 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ, 142.3, 140.8, 140.1, 131.6, 128.8, 128.2, 126.9, 118.6, 81.4, 35.1, 33.5, 28.2, 27.9, 22.3, 13.9. IR (cm^{-1}): 3005, 2982, 2931, 2868, 1706, 1513, 1490, 1336, 1164, 1055, 830. Anal. Calcd for C$_{21}$H$_{26}$BrNO: C, 62.39; H, 6.44; N, 3.47; Br, 19.78. Found: C, 62.88; H, 6.68; N, 3.56; Br, 19.84.

Compound, **10**. The reaction was performed according to the procedure described for the compound **2**. Compound **8**, 2.38 g (4 mmol), compound **9**, 1.62 g (4 mmol), sodium *tert*-butoxide, 0.58 g (6 mmol), Pd(OAc)$_2$, 44.9 mg (0.2 mmol), BINAP, 374 mg (0.6 mmol) in 20 mL of dry toluene, and 15 mL of dry THF were stirred and heated at 100 °C for 20 h. The crude product was purified by chromatography on silica gel eluting with CH$_2$Cl$_2$/hexanes (3:1 with 1% v/v of Et$_3$N) to give 3.3 g (3.6 mmol, 90% yield) of titled compound. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.33 (d, J = 8.4 Hz, 2H), 7.21−7.18 (m, 8H), 7.08 (s, 4H), 6.99−6.93 (m, 9H), 6.76 (dd, J = 8, 2 Hz, 1H), 6.75−6.72 (m, 3H), 6.59 (dd, J = 7.2, 1.6 Hz, 1H), 4.82 (s, 1H), 2.45−2.39 (m, 8H), 1.49−1.43 (m, 8H), 1.42 (s, 9H), 1.27−1.20 (m, 8H), 0.86−0.80 (m, 12H).

Compound, **11**. The same procedure as that used previously was followed using 2.50 g (2.7 mmol) of compound **10**, 1.10 g (2.7 mmol) of compound **9**, 0.39 g (4.1 mmol) of sodium *tert*-butoxide, 30.5 mg (0.14 mmol) of Pd(OAc)$_2$, 82.5 mg (0.41 mmol) of *t*-Bu$_3$P in 30 mL of dry toluene, and 10 mL of dry THF. The crude product was purified by chromatography eluting with CH$_2$Cl$_2$/hexanes (4:1 with 1% v/v of Et$_3$N) to give 3.1 g (2.5 mmol, 92% yield) of titled compound **11**. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.25 (d, J = 8.4 Hz, 4H), 7.19−7.17 (m, 6H), 7.12 (d, J = 2 Hz, 4H), 7.07−7.02 (m, 4H), 7.00−6.96 (m, 15H), 6.89 (t, J = 7.8 Hz, 1H), 6.81 (dd, J = 8, 1.2 Hz, 1H), 6.66 (dd, J = 8, 1.2 Hz, 1H), 2.44 (t, J = 7.8 Hz, 6H), 2.39 (t, J = 7.6 Hz, 4H), 1.51−1.42 (m, 10H), 1.40 (s, 18H), 1.28−1.17 (m, 10H), 0.88−0.80 (m, 15H).

Compound, **12** *(Monomer)*. Compound **11**, 3.50 g (2.8 mmol) was dissolved in 30 mL of trifluoroacetic acid and stirred for 1 h at room temperature. TFA was evaporated and the residue was dissolved in 20 mL of toluene, and 50 mL of 1 M NaOH aqueous solution was added. The mixture was stirred for 20 min and then separated. The aqueous phase was extracted with three 5 mL portions of diethyl ether. The combined organic phases were dried over MgSO$_4$. After the removal of solvents the crude product was purified by chromatography eluting with CH$_2$Cl$_2$/hexanes (1:4 with 1% v/v of Et$_3$N, 1% v/v MeOH) and then with CH$_2$Cl$_2$/hexanes (1:2 with 1% v/v of Et$_3$N) to give a pale-brown resin, 2.1 g (2.0 mmol, 71% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ, 7.22−7.20 (m, 6H), 7.10 (d, J = 8.8 Hz, 4H), 7.06 (d, J = 3.2 Hz, 4H), 7.01−6.92 (m, 11H), 6.85 (d, J = 8.8 Hz, 4H), 6.83−6.76 (m, 3H), 6.77 (d, J = 8.8 Hz, 4H), 4.94 (s, 2H), 2.50−2.41 (m, 10H), 1.57−1.42 (m, 10H), 1.32−1.20 (m, 10H), 0.90−0.81 (m, 15H). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ, 149.9, 149.4, 146.4, 145.9, 143.6, 143.1, 141.7, 141.4, 139.5, 137.4, 137.0, 135.2, 130.0, 129.6, 129.5, 126.4, 125.8, 125.3, 124.8, 124.3, 35.4, 34.2, 22.6, 14.1. IR (cm^{-1}): 3392, 3026, 2956, 2870, 1607, 1506, 1305, 1270, 825. Anal. Calcd for C$_{74}$H$_{83}$N$_5$: C, 85.26; H, 8.02; N, 6.72. Found: C, 84.53; H, 7.75; N, 6.67. M$^+$/z = 1041.7.

Polymerization Procedure. *Polymer, PN*. Polycondensation has been done according to the method of Goodson et al.[10] 7.2 mg (0.032 mmol) of Pd(OAc)$_2$, 19.4 mg (0.096 mmol) of *t*-Bu$_3$P were dissolved in 1 mL of dry toluene under an argon

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atmosphere and stirred for 20 min. Then, 0.798 g (0.767 mmol) of monomer (compound **12**), 0.181 g (0.767 mmol) of 1,3-dibromobenzene, 0.115 g (1.2 mmol) of sodium *tert*-butoxide, and 4 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated to 90 °C for 4 days. The mixture was cooled to room temperature, and polymer was precipitated by transferring the solution into 200 mL of methanol by a pipet. The solid was isolated via filtration and washed with water and methanol. Low-molecular-weight products were removed by extraction with acetone and then with hexanes. The polymer was then dissolved in a small amount of toluene and precipitated in methanol, filtered, and finally dried in a vacuum. The resulting polymer was isolated as white powder. ^{1}H NMR (400 MHz, C_6D_6) δ, 7.13−7.10 (m, 12H), 7.06−7.00 (m, 12H), 6.98−6.92 (m, 12H), 6.81−6.75 (m, 4H), 2.44 (t, J = 7.6 Hz, 10H), 1.52−1.45 (m, 10H), 1.30−1.21 (m, 10H), 0.90−0.83 (m, 15H). ^{13}C NMR (100 MHz, C_6D_6) δ, 149.3, 146.3, 145.7, 143.9, 143.1, 142.9, 142.6, 137.5, 137.2, 129.6, 129.5, 125.8, 124.9, 124.6, 35.4, 34.1, 22.7, 14.2. IR (cm^{-1}): 3400, 3026, 2955, 2926, 2856, 1591, 1502, 1482, 1300, 1266, 828, 774, 696. Anal. Calcd for $C_{80}H_{85}N_5$: C, 86.06; H, 7.67; N, 6.27. Found: C, 85.32; H, 7.53; N, 6.18. M_w = 495 × 10^3 Da, M_n = 99.3 × 10^3 Da, D = 4.98.

Dimer D1. Palladium acetate, 4.7 mg (0.021 mmol) and tri-*tert*-butylphosphine, 12.7 mg (0.063 mmol) were dissolved in 2 mL of dry toluene under an argon atmosphere and stirred at room temperature for 15 min. Then, compound **5**, 0.35 g (0.7 mmol), 1,3-dibromobenzene, 0.082 g (0.035 mmol), sodium *tert*-butoxide, 0.1 g (1.05 mmol), and ca. 8 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated to 110 °C for 20 h. The crude product was purified by chromatography eluting with CH_2Cl_2/hexanes (1:2 with 1% v/v of Et$_3$N) and then crystallized from hexanes/acetone to give 0.35 g (0.32 mmol, 92.4% yield) of **dimer 1**. ^{1}H NMR (400 MHz, C_6D_6) δ, 7.20−7.16 (m, 13H), 7.05 (s, 8H), 6.97−6.92 (m, 13H), 6.80 (dd, J = 8 Hz, 2 Hz, 2H), 2.46−2.41 (m, 12H), 1.52−1.44 (m, 12H), 1.28−1.22 (m, 12H), 0.85 (t, J = 7.4 Hz, 18H). IR (cm^{-1}): 3031, 2956, 2928, 2870, 1607, 1501, 1465, 1314, 1267, 828, 697.

Dimer D2. Dimer 2 was prepared according to the procedure described in ref 31.

Oxidation Procedure. The electrochemical oxidation was monitored by cyclic voltammetry. For these investigations, polymer was dissolved in CH_2Cl_2 (10^{-3} M). The experiments were carried out in a one compartment electrochemical cell in a solution of 0.1 M Bu$_4$NBF$_4$ in CH_2Cl_2 with Ag/0.1 M AgNO$_3$ in acetonitrile as a reference electrode and a Pt counter electrode. Scan rate was 100 mV/s. The surface of Pt disk electrode was 3 mm^2.

The chemical oxidation of **PN** was carried out in an argon atmosphere. In a typical procedure, a 100 μL of 7.3 × 10^{-3} M (molar concentration of the mer) solution of **PN** in dichloromethane was oxidized with the appropriate amount of 1.83 × 10^{-2} M of *tris*(4-bromophenyl)amminium hexachloroantimonate, TBA·SbCl$_6$ solution in butyronitrile. Then, 20 μL of the oxidized solution was diluted with dichloromethane to 10^{-4} M of studied polymer and used for UV−vis−NIR measurements.

Pulsed EPR Nutation Measurements by PEANUT Experiment. Nutation pulsed EPR experiments were performed using a Bruker Elexsys 580 EPR spectrometer in pulsed mode at 7 K. The PEANUT experiment (phase-inverted echo amplitude detected nutation) introduced by Stoll et al.[57]

was used to achieve an optimal resolution of nutation frequencies in the recorded spectra.

The PEANUT experiment is described in Scheme 6. In a typical experiment, the first pulse used was a selective low-

Scheme 6. Pulses Sequence Used for the PEANUT Experiments
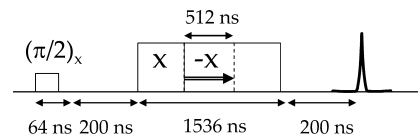
power pulse (typical power $B_1 \approx 0.7$ G, B_1 standing for the amplitude of the magnetic field component of microwave excitation). Two-step phase cycling (+x, −x) was performed on this first pulse. The high-power turning angle pulses (typical power of $B_1 \approx 8.9$ G corresponding to $\nu_{S=1/2}$ = 25 MHz) had a constant length of 1536 ns, and the x pulse (−x pulse) was incremented (decremented) by 256 steps of 2 ns, respectively. At every step, the spin rotary echo was integrated using a 76 ns gate centered at its maximum.

The obtained time-domain oscillating signal was treated with second-order polynomial baseline correction, sinebell transformation, and symmetrical zero-filling (256 zeroes added). Then, it was Fourier transformed using numerical FFT software to yield the corresponding nutation spectrum. Two-dimensional maps (magnetic field vs nutation spectrum) were obtained by successively performing PEANUT experiments at 150 magnetic field values spaced by steps of one Gauss.

The spin multiplicities of detected species were obtained by comparing the measured nutation frequency (ν_{nut}) to the nutation frequency previously measured for a known S = 1/2 system ($\nu_{S=1/2}$) and using the following relationship

$$\nu_{nut} = \sqrt{S(S+1) - m_S(m_S+1)} \cdot \nu_{S=1/2} \tag{1}$$

This relationship is given for an EPR $|S,m_s\rangle \leftrightarrow |S,m_s+1\rangle$ transition and is valid for low microwave power excitation ($g_e\mu_B B_1 \ll D$, where D stands for the axial zero-field splitting parameter of the considered species, g_e stands for the Landé factor of the free electron, and μ_B stands for the Bohr magneton).[58]

SQUID Magnetometry. The SQUID magnetometry experiments were performed with a Quantum Design MPMS XL 5.0 SQUID magnetometer. The frozen solution samples were contained in a quartz tube (4 mm diameter with flat extremity) sealed under vacuum and maintained by a sample quartz sample holder designed to minimize the diamagnetic contribution to magnetization measurements. The residual diamagnetic contributions due to the quartz tube and the sample holder and the diamagnetic magnetization of the solvent (60 μL of chloroform:acetonitrile 1:1 v/v) were measured in blank experiments and were used to remove the diamagnetic contribution from the magnetization measured with solution of the doped polymer.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Voltammograms and differential voltammograms of polymer **PA2** and model compounds **D1** and **D2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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