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ORIGINAL PAPER

In Search of Stable, High-Spin Polymers

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Abstract

Oligomers of poly(thiophene) and poly(*ortho*-phenyleneethynylene) having pendant $S=1/2$ semiquinone radicals (as complexes of cobalt(III)) have been prepared and characterized by electron paramagnetic resonance (EPR) spectroscopy and magnetic measurements (superconducting quantum interferences device = SQUID magnetometry). Our results show that exchange coupling of semiquinone groups along a polythiophene backbone is greater than the corresponding coupling along a poly(*ortho*-phenyleneethynylene) backbone.

1 Introduction

Polyradicals were once thought to be possible inexpensive, lightweight, flexible replacements for inorganic magnetic materials [1–3]. While polyradicals can and have found application in a variety of devices and materials, they are probably not going to replace inorganic materials due in part to high molecular weights and low spin densities, and lack of rational three-dimenional coupling schemes [2, 4–6]. However, polyradicals may be able to find application in spintronics [7–10], organic memory storage devices [11–14], photovoltaics [15–17] and organic batteries [18–25].

The preparation and study of radical-containing polymers spans over three decades [2, 21, 26–29]. Much effort has been focused on coupling the paramagnetic centers along a polymer backbone comprising sp^2- and/or sp-hybridized carbons and heteroatoms. Carbenes [1, 26, 30], triarylmethyl radicals [31–35], amminium radical cations [18, 36–38], nitroxides/nitronylnitroxides [27, 39], galvinoxyl [27, 39–45], phenoxyl [44], and other radicals have been explored as components of such polymers. Lack of stability, spin localization, intermolecular interactions [6, 17, 37, 39,

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40, 43, 46, 47], defects, and other drawbacks have hampered the realization of optimal materials [31, 35, 37, 38, 48–51].

Herein, we describe the reaction of a previously prepared poly(*ortho*-phenyleneethynylene-*ortho*-benzoquinone) (PoPE-BQ, Fig. 1) and its reaction with a cobalt(II) complex ($Co^{II}L_A$) that results in a polymer with pendant cobalt(II) semiquinone groups (PoPE-SQ). We also present the synthesis of oligomers of poly(thiophene) with pendant quinone groups (PTh-BQ, Fig. 1) that also react with the same cobalt(II) complex to produce another semiquinone-containing polymer (PTh-SQ, Fig. 1). Our preliminary investigation is relevant in the search for new high-spin polymers containing redox-active semiquinones which are known to chelate a variety of diamagnetic and paramagnetic metal ions.

2 Results and Discussion

2.1 Semiquinone (SQ)-Containing Polymers

The polymer backbones in PoPE-SQ and PTh-SQ enforce ferromagnetic (high-spin) coupling of SQ spins by virtue of the head-to-tail arrangement of monomeric units as shown in Fig. 2 [39, 40, 42, 52–56]. This connectivity pattern produces nondisjoint spin repeat units along the backbone, and if planar ferromagnetic coupling results.

Additionally, there is great utility in using SQ-containing repeat units since SQs have the capability of chelating a variety of metal ions (both dia- and paramagnetic) [57–60] and SQ complexes are common ligands in several interesting electronic structures, such as mixed valence states, valence tautomerism, and spin crossover [7, 57, 60–65]. These properties allow for introducing new properties and tailoring of resulting polymers' redox activity, three-dimensional structure, conductivity, magnetic interactions, and photophysical properties.

As shown in Fig. 1, the synthesis of the SQ-containing materials is achieved by reaction of PoPE-BQ and PTh-BQ with $Co^{II}L_A$. This reaction proceeds with an attenuation of the BQ C=O stretching in the IR spectra (less than one equiv. $Co^{II}L_A$/BQ unit), or disappearance of the C=O stretching in the IR spectra (≥ 1 equiv.

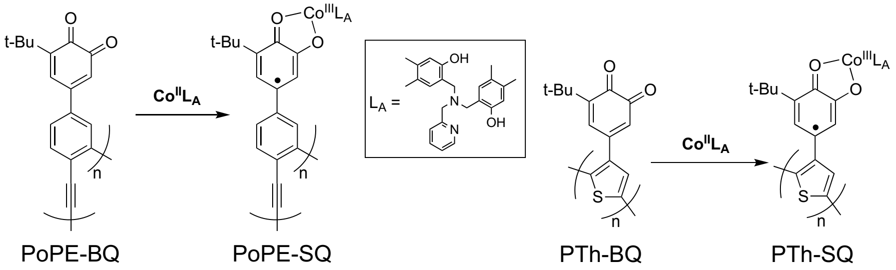

Fig. 1 Structures of polymers presented in this work, and the preparation of SQ-containing polymers from *ortho*-quinone precursors

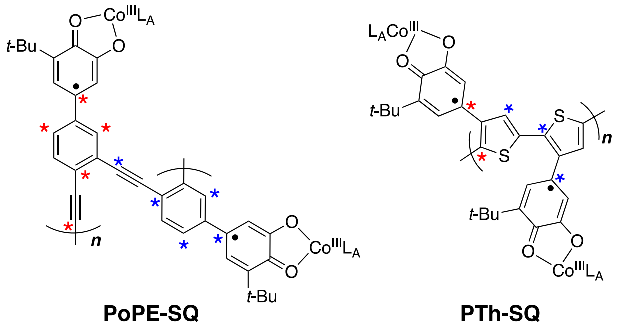

Fig. 2 Spin delocalization in SQ-containing polymers presented in this work. Asterisks denote positive spin densities of the π-system, while the absence of asterisks denote negative spin densities. The alternating positive and negative spin densities enforce ferromagnetic coupling of semiquinone spins along the polymer backbones

$Co^{II}L_A$ /BQ unit), and concomitant appearance of electron paramagnetic resonance (EPR) signals. In the discussion below, SQ-containing polymer labels (PoPE-SQ and PTh-SQ) are appended with "-XXX", where "XXX" denotes the percentage of SQ groups in the polymer, the remainder (100-XXX) is the percentage of unreacted BQ groups.

2.2 Poly(ortho-phenyleneethynylene) (PoPE-SQ)

Synthesis of the PoPE gave oligomers with degrees of polymerization of 17–18. The synthesis (see SI) follows improved steps over the previously reported synthesis [54]. In this work, PoPE-BQ is reacted with $Co^{II}L_A$ complex to generate a PoPE-SQ polymer as shown in Fig. 1. The cobalt (II) reactant was selected due to having favorable redox chemistry with *ortho*-benzoquinone moiety, the product of which is a diamagnetic Co^{III} ion. Moreover, $Co^{III}SQ$ complexes display cobalt hyperfine coupling clearly visible in their room temperature solution EPR spectra [66, 67]. The ancillary ligand, L_A, was selected to be tetradentate to afford more stability to the $Co^{II}L_A$ complex and the resulting PoPE-SQ.

2.3 EPR Spectroscopy

Figure 3a shows the experimental and simulated EPR spectra of $(L_A)Co^{III}$(3,5-di-*tert*-butylsemiquinone) complex as a model compound for the monomer repeat units. The spectrum shows an eight-line splitting pattern due to the $I=7/2$ cobalt nucleus with a hyperfine splitting, $a_{Co}=10.00$ Gauss, and a proton hyperfine with $a_H=3.22$. Figure 3b–d shows the EPR spectra of two PoPE-SQ oligomers. The oligomer in Fig. 3b has a M_n corresponding to five repeat units and has been reacted with an excess of $Co^{II}L_A$, while the oligomer in Fig. 3c shows the spectrum of a polymer with degree of polymerization (DP) = 17–18 repeat units and has been reacted with 0.25 equivalents of $Co^{II}L_A$ ($PoPE\text{-}SQ_{0.25}BQ_{0.75}$ = PoPE-SQ025). In both cases, residual signal due

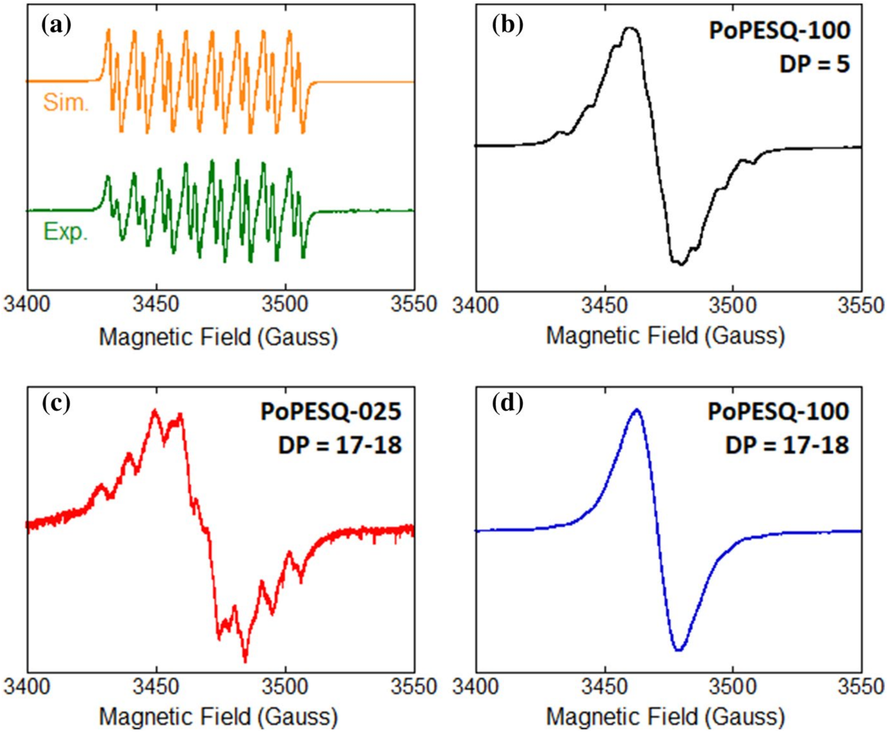

Fig. 3 EPR spectra of **a** (L_A)Co^{III}(3,5-di-*tert*-butylsemiquinone complex. Line splitting: $a_{Co}=10.00$ G, $a_H=3.22$ G. **b** PoPE-SQ (DP=5) that had been reacted with excess $Co^{II}L_A$. **c** PoPE-SQ (DP=17–18) reacted with 0.25 equivalents of $Co^{II}L_A$. **d** PoPE-SQ (DP=17–18) reacted with 1.00 equivalent of $Co^{II}L_A$ per BQ group

to “isolated” (uncoupled) Co^{III}SQ groups can be observed. Figure 3d shows the spectrum of the DP=17–18 PoPE-SQ_1BQ_0 (=PoPE-SQ100) oligomer, having the highest density of Co^{III}SQ groups. Nominally, exchange coupling along the polymer backbone narrows the signal and blurs hyperfine structure. Table 1 shows the results of determining the spin concentration of the PoPE-SQ oligomers by addition of $Co^{II}L_A$. The calculated spin concentration in PoPE-SQ was a close match with the theoretical 85% for entries 1 and 3, 100% for entry 2, and 91% for entry 4. Figure 4a shows the EPR signal from the entries in Table 1, which show increasing signal intensity as more $Co^{II}L_A$ is

Table 1 EPR data for spin concentration calculations

Entry	PoPE (μmol)	$Co^{II}L_A$ (μmol)	Theor. SQ spin concentration per repeat unit	Calc. SQ spin concentration per repeat unit
1	45	12	0.26	0.22
2	45	23	0.51	0.51
3	45	35	0.77	0.64
4	45	46	1.00	0.91

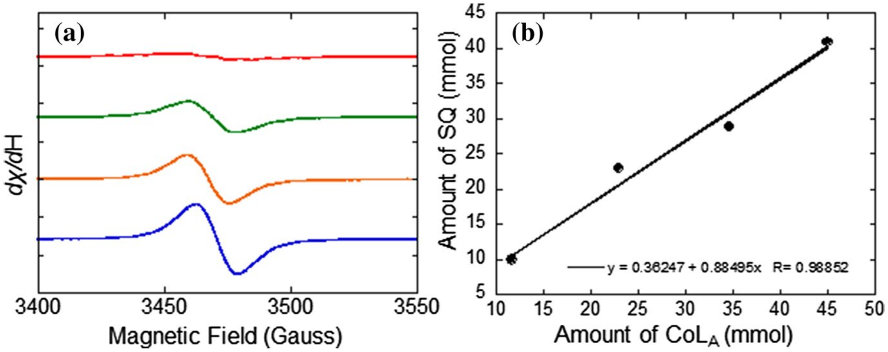

Fig. 4 EPR spectra for the trials of increasing the spin concentration in the polymer as a function of the amount of $Co^{II}L_A$ added. **a** The EPR signal for each trial. **b** Plot of calculated amount of SQ from spin concentration vs. the amount of $Co^{II}L_A$ added

added to generate PoPE-SQ, while Fig. 4b shows the correlation between the amount of SQ EPR signal intensity with the amount of $Co^{II}L_A$ added, indicating that the signal response to the generation of SQs is linear, with an R^2 value of 0.989. This indicates that the through-space intra- or intermolecular antiferromagnetic interactions had minimal effect on the paramagnetic character of the samples in solution. This could be due to the solubility of the samples, as well as the bulky ancillary ligand, L_A, which could be providing enough steric bulk to prevent strong intermolecular interactions.

2.4 Magnetometry

Figure 5 shows the SQUID magnetic data (magnetization divided by saturation magnetization, M/M_{sat}) for PoPE-SQ-050 (50% pendant SQ and 50% pendant BQ) and PoPE-SQ-075 (75% pendant SQ and 25% pendant BQ) alongside the theoretical Brillouin functions for $S = 1/2$, 2/2, 3/2 and 4/2 [68]. As can be seen, the plots of both PoPE-SQ materials roughly follow the $S = 1/2$ Brillouin function with only slight variation at weaker field strengths. This would indicate that the high-spin coupling is not observed for the polyradicals that have been cast into polystyrene ($M_n = 250{,}000$ g/mol) films. This could be due to the polymer chains possibly having aggregated when the polystyrene films were drying and, if the chains are close enough, antiferromagnetic through-space interactions between the chains could be lowering the overall spin of the system. Alternatively, strong bond torsions either along the polymer chain or between the SQ groups and the polymer chain could lower the spin. This was similarly observed for the PTh-SQ polyradicals and will be discussed below.

2.5 Polythiophenes (PTh-SQ)

As with the PoPE-SQ materials, the head-to-tail arrangement of ThSQ units is expected to provide ferromagnetic alignment of SQ spins along the thiophene backbone as shown in Fig. 2.

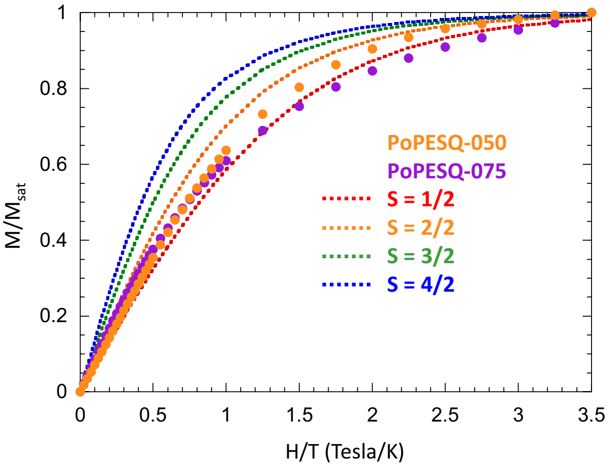

Fig. 5 M/M_{sat} plots for PoPE-SQ-050 and PoPE-SQ-075 in polystyrene films alongside theoretical Brillouin function plots for $S = 1/2$, 2/2, 3/2 and 4/2. Magnetic field was swept from 0.05 to 7 T, while the temperature was held at 2 K

2.6 EPR Spectroscopy

Figure 6 shows the EPR spectra from the monomer radical, $(L_A)Co^{III}$(3-*tert*-butyl-5-thiophenyl-orthosemiquinone) (ThSQ), and 0.25, 0.50, 0.75 and 1 eq. of $Co^{II}L_A$ added to 1 eq. of PTh-BQ (DP ~ 17–18) and stirred for 24 h in CH_2Cl_2 to ensure completion of the reaction. As can be seen, ThSQ shows a doublet of octets, corresponding to the proton hyperfine ($a_H = 3.1$ Gauss) and the $I = 7/2$ cobalt nuclear spin ($a_{Co} = 10.3$ Gauss), similar to those of $(L_A)Co^{III}$(3,5-di-*tert*-butylsemiquinone). As the concentration of SQ groups along the polymer chain increase from 25, 50, 75 and 100%**,** the EPR spectra change: hyperfine becomes broadened and/or merged into a featureless singlet (PTh-SQ100). In the PTh-SQ series, there are two other related changes occurring between the polymers and the monomeric ThSQ that were not observed for the PoPE-SQ oligomers. This is most easily seen in PTh-SQ-025 where the spectral width narrows and smaller hyperfine coupling constants are observed according to the hyperfine coupling as a fraction of the number of coupled radicals ($a_N/2S$) [69]. This, in ThSQ, $a_{Co} = 10.3$ Gauss, but in a triplet dimer the cobalt hyperfine coupling would be $10.3/2 \approx 5.15$ Gauss. This attenuation of the hyperfine coupling leads to an overall smaller spectral width and is indicative of $|J| >> a$, and the presence of spin triplets and quartets. In Fig. 7, these hyperfine couplings are analyzed via stick diagrams to show hyperfine coupling constants that can be ascertained in the spectrum of PTh-SQ-025 beside those for the monomer ThSQ (upper left of Fig. 7). The EPR spectrum of ThSQ has green lines (10.3 Gauss) showing a_{Co} and purple lines to denote a_H (3.1 Gauss). The EPR spectrum for PTh-SQ-025, the outer lines and on the right-hand side of the spectrum, hyperfine couplings of 5.2 and 1.6 Gauss can be observed, which would correspond to two coupled (triplet) SQ radicals interacting through the polymer chain. Nearer to the center of the spectrum,

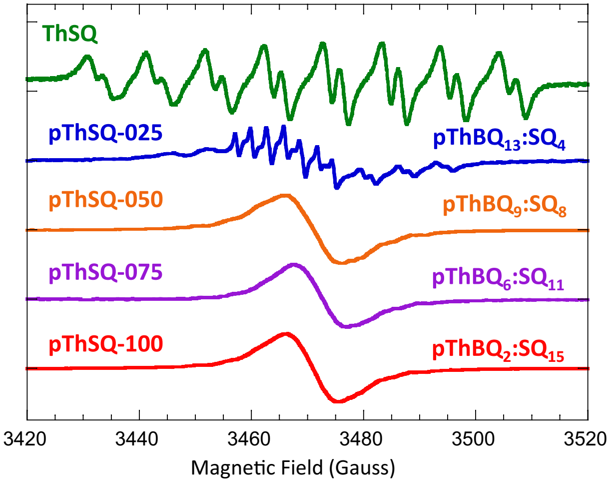

Fig. 6 EPR spectra of a monomer radical (ThSQ) and four polymers that have been reacted with 0.25, 0.50, 0.75 and 1.00 eq. of $Co^{II}L_A$: PTh-SQ-025, PTh-SQ-050, PTh-SQ-075 and PTh-SQ-100, respectively

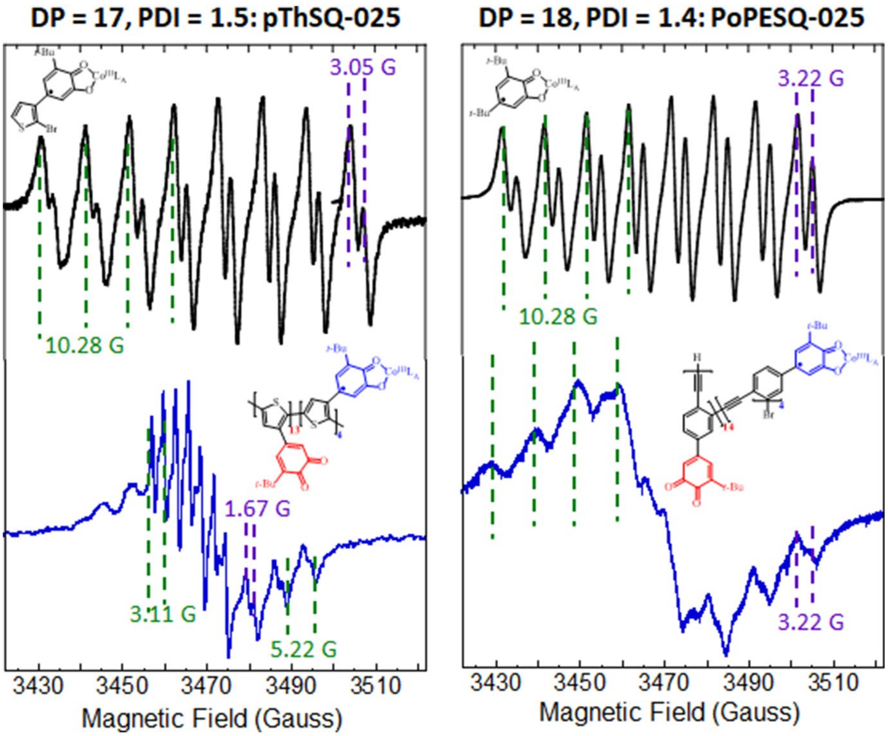

Fig. 7 EPR spectra of ThSQ and PTh-SQ-025 (left) and 3,5-di-*tert*-butylsemiquinone and PoPE-SQ-025 (right). Both polymers are 17 or 18 units long and are both ~ 25% SQ content

hyperfine couplings of approximately 3.1 and 1.0 Gauss can be identified which would correspond to the hyperfine coupling constants for cobalt and the proton due to the interaction with three coupled SQ radicals (quartet) interacting with the nuclei. This is particularly interesting because this is a polymer that only has 25% of its individual monomer units as radicals. From its EPR spectrum, PTh-SQ-025 is dominated by bi- and triradicals, which means for a polymer where only a random 3–4 of the units out of 17 are radicals, the radicals are not only delocalized, but these few radicals are most likely interacting with each other across multiple units. For comparison, the right-hand side of Fig. 7 shows the spectra of $(L_A)Co^{III}$(3,5-di-*tert*-butylsemiquinone) complex and the corresponding PoPE-SQ-025 polymer. PoPE-SQ-025 (bottom right of Fig. 7) displays hyperfine coupling as well from the constituent monomers containing the proton and cobalt nuclei. However, in this case, the 3.2 and 10.3 Gauss hyperfine coupling that was observed in $(L_A)Co^{III}$(3,5-di-*tert*-butylsemiquinone) complex is still the dominant species in the PoPE-SQ-025 polyradical, indicating that the SQ radicals are not interacting strongly with each other. Thus, the EPR data suggest stronger SQ–SQ couplings along a polythiophene backbone compared to a poly(*ortho*-phenyleneethynylene).

2.7 Magnetometry

Figure 8 shows the SQUID magnetic data (magnetization divided by saturation magnetization, M/M_{sat}) for PTh-SQ-025, PTh-SQ-050 and PTh-SQ-075 alongside the theoretical Brillouin functions for $S=1/2$, 2/2, 3/2 and 4/2. As can be seen, the plots of all three PTh-SQ seem to follow the $S=1/2$ Brillouin function with only slight variation at weaker field strengths. This would indicate that the high-spin coordinated coupling is not observed for the polyradicals that have been cast into polystyrene films. The behavior of the PoPE-SQ polyradicals was notably similar. This could be due to the polymer chains possibly having aggregated when the polystyrene films were drying and, if the chains were close enough, antiferromagnetic through-space interactions between the chains could be lowering the overall spin of the system. Alternatively, there could be a high number of head–head (HH) or tail–tail (TT) couplings rather than the desired head–tail (HT), in which two or more separate ferromagnetically coupled segments of one polymer chain cancel each other out. Thus, EPR indicates $J >> a$, and SQUID magnetometry points to $|J| << 1$ K, thus J/k should be in the order of a few mK.

3 Conclusions

Several polyradicals of metallo-semiquinone-containing polymers and oligomers have been synthesized and characterized by EPR spectroscopy and SQUID magnetometry. The EPR spectra of ThSQ, PTh-SQ-025, PTh-SQ-050, PTh-SQ-075 and PTh-SQ-100 indicated coupled radical spins (bi- and triradicals) that could be observed in PTh-SQ-025 and the observed spectral narrowing of PTh-SQ-050, PTh-SQ-075 and PTh-SQ-100 suggests increasing SQ–SQ interactions.

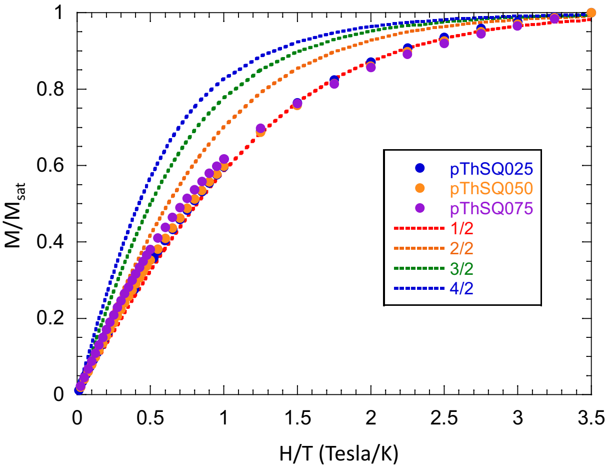

Fig. 8 *M*/*M*$_{sat}$ plots for PTh-SQ-025, PTh-SQ-050 and PTh-SQ-075 in polystyrene films alongside theoretical Brillouin function plots for $S = 1/2$, 2/2, 3/2 and 4/2. Magnetic field was swept from 0.05 to 7 T, while the temperature was held at 2 K

The EPR spin concentration measurements that were performed on PoPE-SQ were unsuccessful for PTh-SQ. PTh-SQ-025 and PTh-SQ-075 were approximately consistent relative to each other, but the PTh-SQ-050 and PTh-SQ-100 were an order of magnitude signal intensity greater. Replicating the polymerization conditions to give polymers that were comparable in terms of molecular weight and polydispersity that were still soluble during post-polymerization transformations to the results shown was challenging and this poor solubility could explain the disparate results in the spin concentration experiments for pThSQ.

Coupled SQ groups could be observed in the EPR spectrum of PTh-SQ-025 to afford at least bi- and triradicals in a polymer that was 17 units long with a random distribution of SQ radicals. This would suggest that many of these radicals were able to interact over two or more thiophene units. Spectral signatures of such SQ–SQ interactions were not observed in PoPE-SQ025.

The results presented here suggest that polythiophene may make a better conjugated polymer backbone for SQ–SQ exchange coupling than does poly(*ortho*-phenyleneethynylene). However, high-spin polymers with $J > 1\ \mathrm{cm}^{-1}$ were not realized according to magnetic measurements. These results together serve as a proof of concept to demonstrate that controlling the amount of organic radical repeat unit by the reduction of quinone with the cobalt complex could be achieved, as indicated by the PoPE-SQ spin concentrations (Fig. 4), and that non-negligible coupling can be achieved between these units, as indicated by the presence of higher spin states in the pThSQ-025 EPR spectrum (bottom left of Fig. 7). We intend to pursue this strategy of cobalt II reduction of quinones to semiquinones within polymer backbones; however, these specific polymer backbones may not be worth further studies due to the challenges of achieving consistent molecular weights and their poor solubilities during post-polymerization modification.

Author Contributions PH and DAS wrote the manuscript. PH prepared and characterized all molecules and polymers.

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Availability of Data and Material Supporting material; synthetic procedures and spectral data.

Compliance with Ethical Standards

Conflict of interest The authors declare no conflicts of interest.

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