A phenalenyl-based neutral stable π-conjugated polyradical

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ABSTRACT

The first neutral π-conjugated polyradical based on phenalenyl with the spin unit inside the main chain was prepared. Cyclic voltammetry studies showed that this polyradical had excellent redox reversibility and enhanced π-delocalization between the neighboring spin units, in consistent with the UV–vis results. Initial magnetic studies showed that a strong antiferromagnetic interaction existed at solid state. The conductivity of the polyradical was measured with a value $\sigma_{RT} \approx 10^{-8}$ S/cm.

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1. Introduction

Single component molecular materials based on neutral stable radical building blocks, displaying intrinsically conductive and magnetic properties [1–5], represent an appealing yet challenging alternative to conventional charge-transfer salts. While their design and synthesis are rather challenging, great progress has been made recently, including many neutral small molecular radicals [6–11] and polyradicals [5,12,13]. In addition to the advantage of processing for practical application, neutral stable polyradicals with high spins represent an appealing strategy to obtain good bulk conductive and magnetic properties. Arbitrarily, neutral stable polyradicals could be cataloged into two types: polymers bearing the pendant spin unit in the arm (**A** in Fig. 1) and having the spin unit inside the main chain (**B** in Fig. 1). For system **A**, the unpaired electron as the spin unit might interact through space or the army and polymer main chain if conjugation can get through and many of these neutral stable polyradicals, such as with pendant nitroxide [12] and phenoxyl [13,14] radical unit, have been reported. For system **B** where the unpaired electron or spin unit stays inside the main chain, direct spin coupling and the singly occupied molecular orbital (SOMO) overlapping of the radical unit can be facilitated through the conjugated main chain. This may include the magnetic

poly(1,3-phenylenephenylmethine)s with magnetic ordering and a huge magnetic moment (spin quantum number $S > 5000$ at 3.5 K) at low temperature [5]. We argue that for better solid-state properties, system **B** would be more desirable.

Phenalenyl (PLY) radical family belongs to odd alternant hydrocarbons with completely planar π conjugation [1,2,8,15]. Planar electron spin delocalization through the planar π system has made most of PLY radicals persist indefinitely, in many cases despite lack of an appreciable steric barrier [6,16–24]. The on-site Coulomb barrier (U) for charge-transfer in this family is so far the smallest compared with other neutral stable radical families and the strong π–π interaction between the neighboring molecular SOMO can form continuous conducting path in the solid state [17]. These characteristics have made them the best neutral organic radical conductor of those previously reported [2,5,18]. We are interested to use these stable PLY neutral radicals as building blocks to prepare polyradicals of type **B**, where in addition to the expected gain of polymer processing and enhanced stability, we hope that the intendance for σ or π dimmer formation [2,5,19] of many planar conjugated radical molecules can be diminished, and more importantly, better solid-state conducting and magnetic properties could be produced due to the forced cooperative interaction between the radical units [9,10,20]. Recently, we have reported the first PLY-based polyradical of type **A** and its photovoltaic application [16,25]. Herein we report the preparation of the first neutral stable polyradical **3** (Scheme 1) of type **B** with planar π conjugated PLY radical unit inside the polymer main chain.

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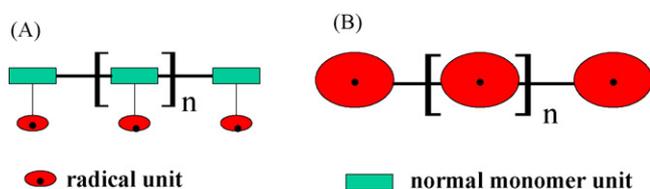
Fig. 1. Two types of neutral stable polyradicals. (**A**) Polymers bearing the pendant spin unit in the arm; (**B**) polymers having the spin unit inside the main chain.

2. Experimental

2.1. Reagents and instruments

Boron trichloride (Aldrich) and cobaltocene (Acros) were all commercial products and were used as received. 1,4-diethynyl-2,5-bis(octyloxy)benzene [26], 9-hydroxy-5-iodo-1-oxophenalene [27] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) [28] were prepared using procedures reported in the literatures. All manipulations were carried out under a dry argon

Scheme 1. Synthesis of the monomer **1⁺TFPB⁻** (a) and polyradical **3** (b).

atmosphere using standard Schlenk techniques, and solvents were purified by standard procedures. ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts were recorded in ppm relative to the internal standard TMS. Mass spectra were recorded on a LCQ Advantage spectrometer with ESI resource. HRMS were recorded on a VG ZAB-HS mass spectrometer with ESI resource. MALDI-TOF MS analysis was performed on a Bruker BIFLEX III mass spectrometer. IR and UV–vis–NIR spectra were obtained using Bruker–Tensor 27 and JASCO-V570 spectrometers, respectively. Elemental analyses were measured using a Yanaca CDRDER MT-3 instrument. Gel permeation chromatography (GPC) analysis was performed on a Waters 510 system using polystyrene as the standard and THF as eluent at a flow rate of 1.0 mL min^{-1} at 40 °C. Cyclic voltammetric measurement was performed on a LK98BII Microcomputer-based Electrochemical Analyzer, using a Pt wire electrode with n-Bu$_4$NPF$_6$ as the supporting electrolyte, with a Ag/Ag⁺ reference electrode. Magnetic susceptibility was measured with a Quantum Design MPMS-7 SQUID magnetometer from 2 to 300 K at a field of 0.5 T, the magnetization was measured from 0 to 7 T at 1.8 K. The raw data were corrected for both the magnetization of the sample holder alone and the Pascal diamagnetic contribution of the sample itself. ESR studies were performed with a Bruker EMX-6/1 spectrometer on the loose packed powder. The conductivity measurement was performed on Keithley 2612 Soure Measure Unit using the standard 4-probe method on a sample strip made from the powder by pressure.

2.2. Synthesis of monomers and polymer

The synthetic route of the monomers and polymer is shown in Scheme 1a and b. The detailed synthetic procedures are as follows.

2.2.1. 5-iodo-9-N-Octyl-1-oxophenalene

A mixture of 9-hydroxy-5-iodo-1-oxophenalene (1.35 g, 4.0 mmol) and octylamine (5 mL) was stirred in dichloromethane (60 mL) at room temperature for 12 h. The resulting solution was concentrated to 5 mL, and MeOH (50 mL) was added to precipitate a pale yellow powder. Isolation by filtration yielded the title compoud (1.64 g, 95%). MS (ESI): m/z 434.33 (M⁺ + 1). Anal. Calcd. for C$_{21}$H$_{24}$INO: C, 58.21; H, 5.58; N, 3.23. Found: C, 58.47; H, 5.51; N, 3.18. ^{1}H NMR (CDCl$_3$): δ 12.22 (b, 1H), 8.14 (s, 1H), 8.10 (s, 1H), 7.84 (d, 1H), 7.72 (d, 1H), 7.18 (d, 1H), 6.94 (d, 1H), 3.53 (b, 2H), 1.82 (b, 2H), 1.51–1.28 (b, 10H), 0.88 (t, 3H).

2.2.2. Preparation of **1⁺Cl⁻**

5-Iodo-9-N-Octyl-1-oxophenalene (0.65 g, 1.5 mmol) in toluene (40 mL) was treated with boron trichloride in o-xylene (0.75 mL, 0.75 mmol) under argon in the dark, and the mixture was refluxed for 4 h. The yellow solid was isolated by filtration (0.45 g, 65%). MS (ESI): m/z 875.58 [(M−Cl⁻)]⁺. IR (KBr, 4000–400 cm^{-1}): 2923 (m), 2849 (m), 2354 (m), 2328 (w), 1623 (s), 1562 (s), 1513 (m), 1453 (w), 1440 (vw), 1417 (vw), 1397 (w), 1349 (m), 1292 (s), 1243 (m), 1182 (m), 1141 (vw), 1119 (vw), 1103 (w), 1022 (s), 974 (vw), 931 (vw), 883 (w), 828 (m), and 755 (w).

2.2.3. Preparation of **1⁺TFPB⁻**

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) (1.06 g, 1.2 mmol) in ether (3 mL) was added to a dichloromethane (40 mL) solution of **1⁺Cl⁻** (0.92 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by chromatography (SiO$_2$, petroleum/ethyl acetate 3:1), yielding 0.98 g, 56%. MS (ESI): m/z 875.46[(M−TFPB⁻)]⁺. IR (KBr, 4000–400 cm^{-1}): 2929 (m), 2860 (m), 2336 (m), 2338 (m), 1625 (s), 1567 (s), 1517 (m), 1479 (w), 1459 (w), 1415 (vw), 1395 (w), 1353 (s), 1278 (s),
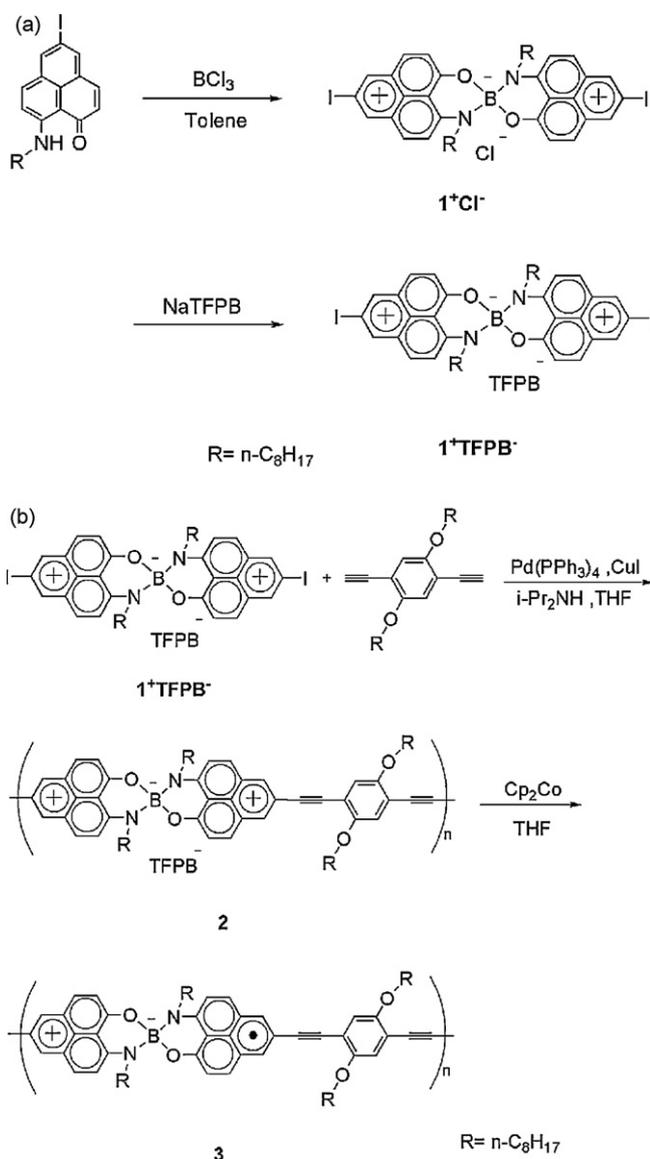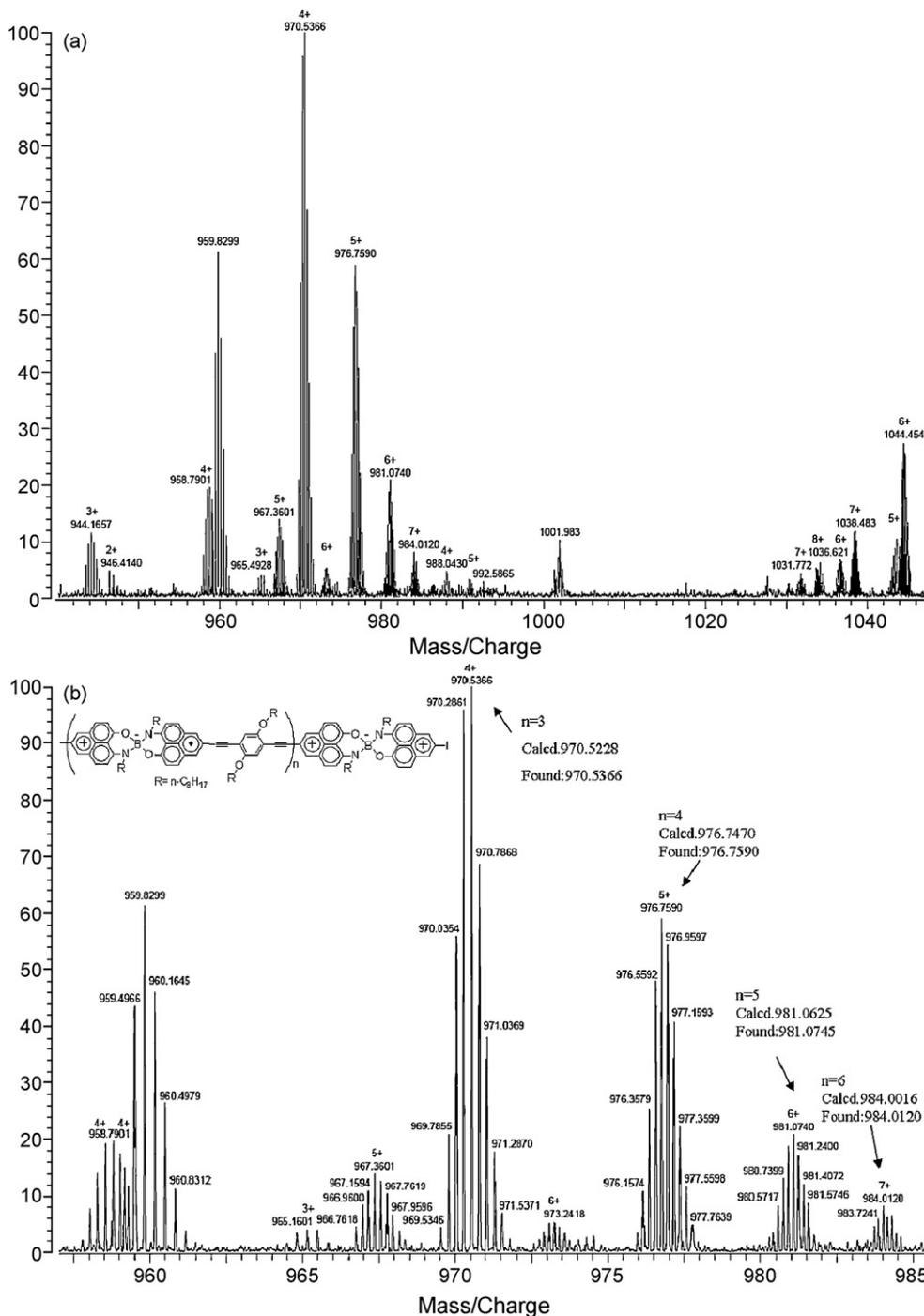
Fig. 2. HR ESIMS of the polymer salt **2**. (a) is the full spectrum of the ESI MS. (b) is the partially enlarged one. Not all peaks are assigned. But we can see the peaks corresponding to DP = 4, 5, 6, 7 and 8. For example, HRMS (ESI), Calcd. 984.0924 for M^{7+} Found, 984.0120 corresponding to DP = 7 (n = 6, plus one ending PLY unit) olilgomer. The m/z difference between each series of peaks was corresponding to the polymerization repeat unit of 1001.65 (Calcd. 1001.63).

1245 (m), 1126 (s), 1032 (m), 883 (m), 838 (m), 750 (w), 713 (m), 684 (m), 668 (m). ^{1}H NMR (CDCl$_3$): δ 8.61 (s, 2H), 8.45 (s, 2H), 8.32 (d, 2H), 8.19(d, 2H), 7.69 (s, 8H), 7.48 (s, 4H), 7.36 (d, 2H), 7.22 (d, 2H), 3.56 (b, 2H), 3.22 (b, 2H), 1.65 (b, 4H), 1.03 (vb, 20H), 0.76 (t, 6H). Anal. Calcd. for C$_{74}$H$_{64}$B$_2$F$_{24}$I$_2$N$_2$O$_2$: C, 50.94; H, 3.70; N, 1.61. Found: C, 51.09; H, 4.00; N, 1.67.

2.2.4. Preparation of polymer 2

A three-neck round bottle was charged with **1$^+$TFPB$^-$** (348 mg, 0.2 mmol), 1,4-diethynyl-2,5-bis(octyloxy)benzene (80 mg, 0.21 mmol), tetrakis-(triphenylphosphine) -palladium (12 mg, 0.01 mmol) and copper iodide(4 mg, 0.02 mmol). THF (10 mL) and diisopropylamine (0.2 mL) were successively added by syringe, and the mixture was stirred at 45 °C for 72 h. The cooled reaction mixture was filtered and then precipitated in 80 mL ether, filtered, washed with ether (3 × 10 mL), acetonitrile (3 × 10 mL) and ether again to yield 130 mg polymer **2**, 35%. IR (KBr, 4000–400 cm^{-1}): 2918 (s), 2853 (m), 2359 (m), 2329 (m), 1624 (s), 1592 (s), 1576(s), 1521 (s), 1461 (m), 1395 (m), 1349 (s), 1293 (s), 1276 (s), 1208 (w), 1178 (w), 1159 (vw), 1125 (s), 1026 (s), 944 (vw), 891 (m), 827 (m), 709 (w), 680 (m), 668 (m). HRMS (ESI), Calcd. 984.0924 for M^{7+}, Found, 984.0120 (corresponding to DP = 7 oligomer). MALDI-TOF:

HRMS (ESI), Calcd. 5886 for M$^+$ Found, 5885 (corresponding to DP = 5 oligomer without the countanion **TFPB$^-$**).

2.2.5. Preparation of polyradical 3

Cobaltocene (15 mg, 0.08 mmol) was dissolved in THF (10 mL) and filtered, the filtration was added to a THF solution (30 mL) of the polymer **2** (75 mg, 0.04 mmol per unit). The mixture was stirred for 12 h. The black precipitate was filtered and washed thoroughly with THF (15 mL × 4 mL) and acetonitrile (15 mL × 4 mL), yielded 31 mg polyradical **3**, 78%. IR (KBr, 4000–400 cm^{-1}): 2922 (m), 2853 (m), 2357 (m), 2332 (m), 1624 (w), 1589 (s), 1505(s), 1464 (m), 1432 (s), 1413 (s), 1372 (vw), 1343(m), 1272 (s), 1210 (m), 1176 (w), 1002 (s), and 812(w).

3. Results and discussion

3.1. Synthesis and characterization of polyradical

The synthesis of the key salt monomer **1$^+$TFPB$^-$** and its precursor **1$^+$Cl$^-$** followed the procedures in the literature [19]. **1$^+$TFPB$^-$** was obtained by the counterion exchange of **1$^+$Cl$^-$** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB). The **TFPB$^-$** anion was used to achieve the required solubility for both the monomers and the following polymer **2** (Scheme 1), and indeed **1$^+$TFPB$^-$** has an excellent solubility in many common organic solvents, such as ether, THF, toluene, etc. It is worthy to note that this salt **1$^+$TFPB$^-$** could be purified by chromatography. The good solubility and purity enable the following polymerization reaction to go through smoothly.

The precursor polymer salt **2** for polyradical **3** was synthesized via Sonogashira–Hagihara coupling reaction between the monomer salt **1$^+$TFPB$^-$** and 1,4-diethynyl-2,5-bis(octyloxy)benzene as described in Scheme 1. Polymer salt **2** was rather soluble in THF, CH$_2$Cl$_2$, CHCl$_3$, DMF, but insoluble in CH$_3$CN. The number averaged molecular weight, polydispersity and the degree of polymerization of polymer **2** were $M_n = 1.3 \times 10^4$, PDI = 1.3, and DP ≈ 8, respectively, using GPC calibrated relative to polystyrene standards (Figure S1 in SI). The ESI-HRMS of **2** showed a series of peaks corresponding to its oligomers, also confirmed by MALDI-TOF result (Fig. 2 and Figure S2). The m/z difference between each series of peaks was corresponding to the polymerization repeat unit. The black powder polyradical **3** was obtained by bulk reduction of the polymer **2** with cobaltocene.

3.2. Electrochemical properties

Cyclic voltammetry (CV) of the polymer salt **2** (Fig. 3) showed two reversible but broad reduction process, with half-wave $E^1_{1/2}$ and $E^2_{1/2}$ reduction potential around −0.84 and −1.25 V vs Ag/Ag$^+$ in corresponding to the expected triad of oxidation states: a reversible (+1/0) and (0/−1) wave, respectively. The reduction (at ∼−0.9 V) and oxidation (at ∼−1.2 V) peaks of the polyradical contain side (multiple) peaks, indicating the possible multiple reduction and oxidation process induced by the π-conjugation and delocalization between the neighboring spiro-phenalenyl and diyne units. CV of the monomer salt **1$^+$TFPB$^-$** gave well-behaved reversible double reduction corresponding to the successive generation of radical and anion and the half-wave values ($E^1_{1/2} = -0.81$ V, $E^2_{1/2} = -1.30$ V vs Ag/Ag$^+$) were close to the reported phenalenyl based N,O-ligand small molecular systems [18,20,22–24]. The low dispro-portionation potential of **2** calculated from $\Delta E^{2-1} = E^2_{1/2} - E^1_{1/2} = -0.49$ eV is similar to that of the PLY small molecular compounds. The value largely determines the on-site Columbic correlation energy in the solid state and is an important discriminator for

organic metals. Thus, cobaltocene was chosen to reduce the polymer salt **2** because its oxidation potential falls between the $E^1_{1/2}$ and $E^2_{1/2}$ reduction potential of not only the polymer salt **2**, but also the monomer **1$^+$TFPB$^-$**.

3.3. The UV–vis spectra of 1$^+$TFPB$^-$, 2 and the polyradical 3

The UV–vis spectra of **1$^+$TFPB$^-$**, **2** and the polyradical **3** (Fig. 4) all showed an absorption peak at about 395 nm. While the absorption $\lambda_{max} = 275$ nm from the monomer **1$^+$TFPB$^-$** was bathochromically shifted to 327 nm (**2**) and 329 nm (**3**), respectively. Compared with the monomer salt **1$^+$TFPB$^-$**, the polymer salt **2** has a new peak around 688 nm. This indicates that there are significant π-conjugation and delocalization between the neighboring spiro-phenalenyl and diyne units. More importantly, a new and very broad absorption of the polyradical **3** emerged with $\lambda_{max} = 892$ nm in comparison with that ($\lambda_{max} = 688$ nm) of **2**. This peak might also come from the bathochromic shift of the peak at 688 nm for polymer salt **2**, indicating much better π-conjugation happens along the polymer main chain for the polymer radical **3** compared with that in the salt polymer **2**. There is no significant absorption above 800 nm for of the monomer **1$^+$TFPB$^-$** and the polymer salt **2**.
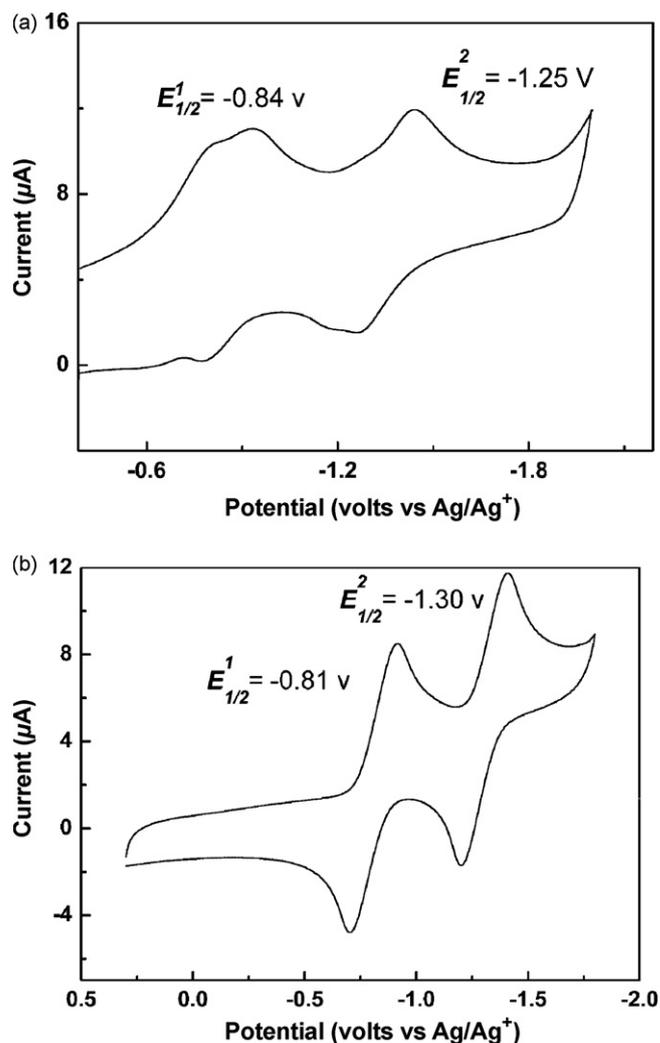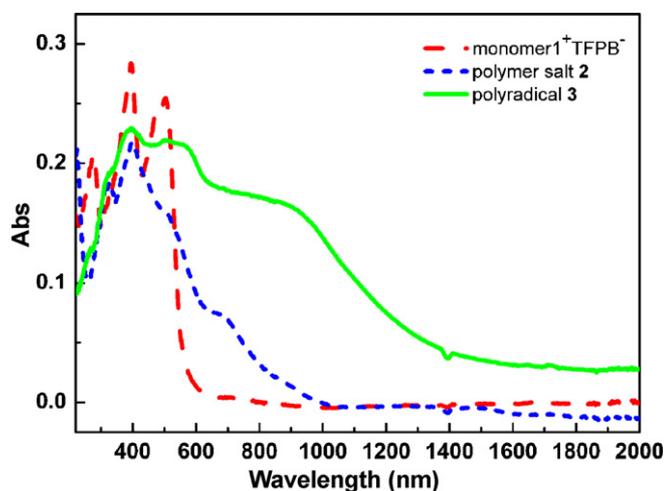

Fig. 3. Cyclic voltammetry of (a) polymer salt **2** in CH$_2$Cl$_2$, referenced to Ag/Ag$^+$ via internal ferrocene (0.21 V) in CH$_2$Cl$_2$; (b) monomer salt **1$^+$TFPB$^-$** in CH$_2$Cl$_2$, referenced to Ag/Ag$^+$ via internal ferrocene (0.21 V).
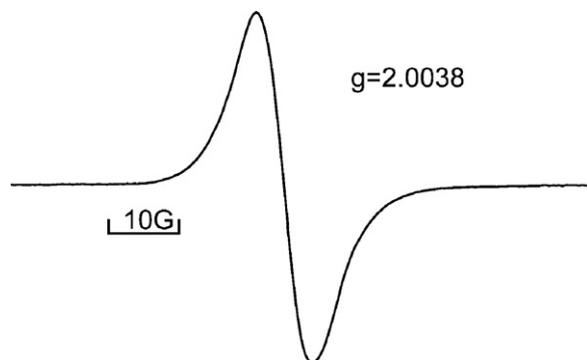
Fig. 4. UV–vis spectra (solid power with $BaSO_4$) of monomer **1^{+}TFPB^{-}**, polymer **2** and polyradical **3**. They showed absorption maximum at about 395 nm. While the absorption at $\lambda_{max} = 275$ nm of the **1^{+}TFPB^{-}** was bathochromically shifted to 327 nm (**2**) and 329 nm (**3**), respectively. A new and very broad absorption of **3** emerged with $\lambda_{max} = 892$ nm in comparison with **2** ($\lambda_{max} = 688$ nm), which indicated a significantly increased π-conjugation delocalization in the polyradical **3**.

Fig. 6. Magnetic susceptibility (χ_{mol}) (A, red square) and $\chi_{mol}T$ (B, green diamond) of polyradical **3** as a function of temperature (K). χ_{mol} is the molar paramagnetic susceptibility based on average 8 repeating units, which was corrected by subtraction of the Pascal diamagnetic contribution and the diamagnetic contributions of sample holder. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).
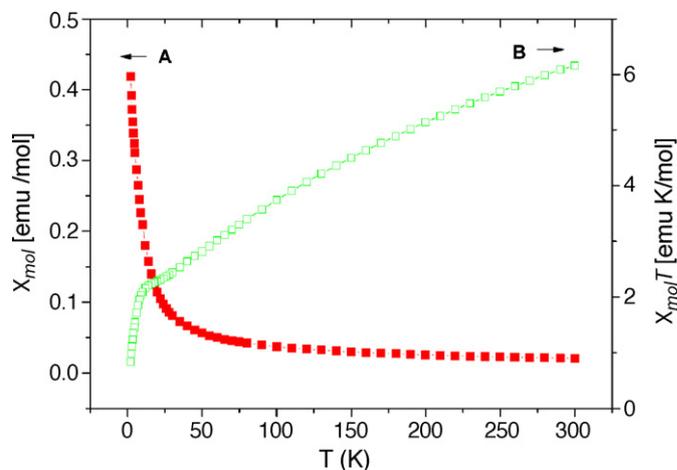
3.4. ESR spectrum, magnetism, conductivity

The ESR spectrum (Fig. 5) of polyradical **3** shows a unimodal but broad peak at $g = 2.0038$ with sweep width = 42 G. The values are close with that of PLY radicals [15]. ESR monitoring showed the polyradical **3** was very stable in the absence of air in solution and in the solid state even exposed to the air for weeks.

The paramagnetic susceptibility (χ) of the polyradical **3** was measured using a Quantum Design MPMS-7 SQUID magnetometer from 2 to 300 K at a field of 0.5 T. The molar magnetic susceptibility χ_{mol} (assuming average 8 repeating units) of polyradical **3** was corrected by subtraction of the Pascal diamagnetic core contributions (-4858.3×10^{-6} emu/mol) and the diamagnetic contributions of sample holder from the measured magnetic susceptibility. The χ_{mol} and $\chi_{mol}T$ are plotted with temperature (T) in Fig. 6. In the high temperature range (>100 K), the Curie–Weiss law $\chi_{mol} = C/(T - \theta)$ fitting gives a Curie constant $C = 9.36$ emu K/mol and Weiss constant $\theta = -158.4$ K. The Curie constant is corresponding to a *ca.* spin quantum number $S = 8/2$ and matching the average repeating unit of 8 in the polymer. This indicates that high-spin polyradicals could be made using PLY radical building block. The $\chi_{mol}T$ vs T plot (Fig. 6B) decreases considerably from 300 to 10 K, and even more rapidly below 10 K. Combined with the large negative Weiss constant, this indicates there is a strong antiferromagnetic

interaction between the spins at low temperature. We also want emphasize that the possible trace amount of magnetic materials due to the reducing agent Cp2Co may complicate the magnetic data above.

The four-probed conductivity of the powder strip prepared with pressure in a home-made model for polyradical **3** was measured with a value $\sigma_{RT} \approx 10^{-8}$ S/cm, considerably lower than that of the reported single-crystal conductivity of the corresponding PLY small molecular radicals [19–24]. Partial reason of this lower conductivity compared with that of the single-crystal PLY small molecular radicals of course is due to the nature of the powder state of polyradical **3**, which could be confirmed by the result of its X-ray diffraction (XRD) analysis (see Figure S3), in which no obvious peak was observed and the polyradical **3** existed in a disorderly state. On the other hand, XRD analysis of polymer salt **2** (see Figure S4) showed two strong peaks at $2\theta = 21.1°$ and $21.5°$ with d value 4.21 Å and 4.14 Å, respectively, indicating there was weakly π-π stacking interaction between aromatic rings of the polymer chains. The conductivity ability would increase with high scope if orderly structure of the polyradical **3** could be obtained. On the other hand, we suspect that the block of connecting C≡C and phenyl fragment between the polymerized PLY units might have impact on the intrinsic low conductivity too. Modification of the polymer structure is underway and will be reported later.

4. Conclusion

We have prepared the first phenalenyl-based neutral π-conjugated polyradical. Cyclic voltammetry and UV–vis studies show that there is significant π-delocalization between the neighboring radical units. Initial magnetic studies show a strong antiferromagnetic (through interchain or intrachain) interaction existed in the solid polyradical. Although the conductivity is low, we are optimistic that our approach using planar PLY radical unit as building block for π-conjugated polyradicals will eventually lead to neutral stable polyradical materials with improved conductivity and/or charge mobility. So far, the insolubility of this polyradical has hampered us in these works, including the measurement of its charge mobility. This issue and other polyradicals in this family for better solid-state properties are currently being investigated and the results will be reported soon later.

Fig. 5. ESR spectrum of the polyradical **3** as a powder sample at room temperatrure, $g = 2.0038$, sweep width = 42 G. The values of g and sweep width are similar with small molecular PLY radicals in literature.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2009.05.025.

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