# **Processable Hybrids of Ferrocene-Containing Poly(phenylacetylene)s and Carbon Nanotubes: Fabrication and Properties**

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A group of ferrocene-containing poly(phenylacetylene)s (PPAs) with different alkyl spacers were synthesized by using organorhodium complexes  $[Rh(diene)Cl]_2$  and  $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$  as catalysts. With the aid of  $\pi - \pi$  interactions between the walls of carbon nanotubes (CNTs) and the PPA skeleton together with the ferrocene pendants, the polymer (P1, P2(5) and P2(10)) chains effectively wrapped round the shells of both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs). The "additive effect" of the PPA skeleton and the ferrocene pendants in dispersing the SWNTs and MWNTs resulted in the generation of highly soluble hybrids. The solubilities of P1-functionalized SWNTs and MWNTs in tetrahydrofuran (THF) are up to 633 mg/L and 967 mg/L, respectively. They are much higher than the solubilities of M1-modified SWNTs and MWNTs, which are only 167 mg/L and 133 mg/L in THF. The results indicate the existence of a powerful polymer effect on dispersing CNTs. The high solubilities of the hybrids in organic solvents allowed us to fabricate high-quality and large-area films. Meanwhile, the desirable loading of ferrocene-containing PPAs onto the CNTs offered polymer/CNTs hybrids with multiple redox centers and ferrocene-featured electrochemical properties. The P1/MWNT hybrid exhibits evident optical-limiting properties. At high incident laser fluence, the optical-limiting power of P1/MWNT is higher than that of  $C_{60}$ , a well-known optical limiter. Thermal analyses indicate that the decomposition temperatures ( $T_d$ , the temperature at which a sample loses its 5% weight) for P1 and P1/MWNT are 342 and 346 °C, respectively, much higher than that for PPA (225 °C). Thus the attachment of a ferrocene pendant to a PPA backbone, followed by hybridization with CNTs, improved the thermal stability. Upon pyrolysis, both the polymer and the polymer/CNTs hybrid gave rise to superparamagnetic ceramics; the saturation magnetizations  $(M_s)$  of the ceramics derived from P1 and P1/ MWNT are 29.9 and 26.9 emu/g, respectively. The latter datum is in the list of the best results reported for the magnetic nanocomposites obtained by the attachment of magnetic nanoparticles onto CNTs.

### Introduction

Since their discovery, carbon nanotubes (CNTs) have attracted great attentions in scientific research and technological innovation because of their unique electronic, physicochemical, and mechanical properties, which render them ideal candidates for the fabrication of new-generation optoelectronic devices.<sup>1–7</sup> There are many successful examples showing that their remarkable electronic and optical properties have promised much potential for such high-tech applications as nanosensors, nanoelectrochemical devices.<sup>8–16</sup> Individual CNTs, however, because of their high molecular weights, strong hydrophobicity,  $\pi - \pi$  stacking, and van der Waals attraction, are tightly held together in bundles. This makes CNTs insoluble in any solvents, and thus hampers not only the research of their solution properties, but also their practical applications.

In the past decade, many efforts have been made to endow the CNTs with good solubility in organic solvents or aqueous media. To date, two approaches, covalent<sup>7</sup> and noncovalent<sup>17–20</sup> functionalizations, have been widely used to improve the macroscopic processability of CNTs. Compared with the covalent approach, the noncovalent method enjoys the superiority of not disturbing the electronic structure of CNTs, which is crucial in the fabrication of high-quality optoelectronic devices. Noncovalent functionlization of CNTs with conjugated polymers is regarded as promising in creating new functional nanohybrids since it not only provides a chance to combine the advantages of both, but also affords an opportunity to generate novel characteristics.<sup>18,21</sup>

As a prototypical conjugated polymer, polyacetylene and its substituted derivatives, particularly the derivatives of poly-(phenylacetylene) (PPAs), exhibit a variety of functions.<sup>22,23</sup> One research interest in our group is to create new macroscopically processable and functional PPA/CNT materials with combined advantages of the two components. Previously, we successfully obtained PPA/CNT nanohybrids via the noncovalent approach.<sup>18a,b</sup> A PPA/multiwalled carbon nanotube (MWNT) nanocomposite<sup>18a</sup> was prepared by in situ polymerization, and hybrids of pyrene-

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## SCHEME 1



**SCHEME 2** 



containing PPA/MWNTs<sup>18b</sup> were generated through physical blending. All the hybrids show good functionalities such as optical-limiting property, light-emitting behavior, and efficient photoinduced charge transfer performance.

In this contribution, we present facile synthetic routes to PPAs bearing ferrocene motifs (see Scheme 2, P1, P2(5), and P2(10)) and the preparation of hybrids of P1/single-walled carbon naotube (SWNT) and P1/MWNT. It is well known that ferrocene is a famous mediator in electrochemical detections and biosensors.<sup>24-26</sup> It can be used in the detection of DNA, dopamine, ascorbic acid, hydrogen peroxide,<sup>24,25</sup> and selective recognition of anions.<sup>26a</sup> It is also a very good electron donor, which can be applied in the construction of donor/acceptor ensembles for photovoltaic devices.<sup>3</sup> Chemically modified CNTs by ferrocene-bearing small molecules have been reported by Prato and co-workers; therein, intramolecular electron transfer was observed.<sup>15</sup> Herein, a group of ferrocene-containing PPAs were synthesized, and their structures and properties were characterized and evaluated by gel permeation chromatography (GPC), IR, NMR, thermogravimetric analysis (TGA), UVvisible spectroscopy (UV-vis), and cyclic voltammetry (CV). Through simple physical mixing, ferrocene-containing conjugated polymer/CNT nanohybrids were successfully obtained. The hybrids showed high solubility in common organic solvents, good film forming ability, evident optical-limiting property, and desirable redox activity. Electron transfer between P1 and CNTs was also detected by CV analysis, indicating potential applications in photovoltaic devices. Because of the existence of ferrocene motifs, the pyrolytic products of both P1 and P1/MWNT displayed excellent superparamagnetic behavior.

## **Experimental Section**

Materials. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use. Dichloromethane (DCM) was distilled under normal pressure over calcium hydride under argon before use. Triethylamine (TEA) was distilled and dried over potassium hydroxide. Butane-1,4-diol (4), diethyl ether and methanol (analytical grade) were used directly. MWNTs (90% purity, Strem Chemicals) and SWNTs (Strem Chemicals) were used directly. Ferrocenecarboxylic acid (3) was purchased from Yixing Weite Petrochemical Additives Plant (China). p-Toluenesulfonic acid monohydrate (TsOH), N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were all purchased from Aldrich and used as received without further purification. Rhodium (I) complexes  $[Rh(nbd)Cl]_2$  (nbd = 2,5norbornadiene),  $[Rh(cod)Cl]_2$  (cod = 1,8-cyclooctadiene), and  $Rh^{+}(nbd)[(\eta^{6}-C_{6}H_{5})B^{-}(C_{6}H_{5})_{3}]$  were prepared by literature methods.<sup>27,28</sup> 4-Ethynylbenzonic acid (6), 6-(4-ethynyl-phenoxy)hexanoic acid [7(5)] and 11-(4-ethynylphenoxy)undecanoic acid [7(10)] were synthesized according to our previously published procedures.18b

**Instrumentation.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker ARX 500 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS;  $\delta = 0$  ppm) as the internal standard. IR spectra were recorded on a Bruker VECTOR 22 spectrometer. UV-vis absorption spectra were measured on a Varian CARY 100 Bio UV-visible spectrophotometer. The thermal stability of the polymers was evaluated on a Perkin-Elmer Pyris thermogravimetric analyzer TGA 6. Molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indexes ( $M_w/$  $M_n$ ) of the polymers were estimated THF by a Waters Associates GPC system. A set of monodisperse polystyrene standards covering molecular weight range of  $10^3-10^7$  was used for molecular weight calibration.

Scanning electron microscope (SEM) images of the polymerwrapped CNTs were taken on a JEOL 6300L field emission SEM operating at an accelerating voltage of 5 kV, while their transmission electron microscope (TEM) images were recorded with a JEOL/JEM-200 CX TEM at an accelerating voltage of 160 kV. The X-ray photoelectron spectroscopy (XPS) experiments were conducted on a PHI 5600 spectrometer (Physical Electronics), and the core level spectra were measured using a monochromatic Al K $\alpha$  X-ray source (hv = 1486.6 eV). The analyzer was operated at 23.5 eV pass energy, and the analyzed area was 800  $\mu$ m in diameter. The binding energies were referenced to the adventitious hydrocarbon C 1s line at 285.0 eV, and the curve fitting of the XPS spectra was performed using the least-squares method. The energy-dispersive X-ray (EDX) analyses were performed on a Philips XL30 SEM system with quantitative elemental mapping and line scan capacities operating at an accelerating voltage of 15 kV. Optical-limiting experiments were carried out at 532 nm, using 8 ns optical pulses generated from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near Gaussian transverse mode with a repetition rate of 10 Hz. The pulsed laser beam was focused onto a 1 mm square quartz cell. The incident and transmitted energies were measured by an OPHIR detector (30-A-Diff-SH). Cyclic voltammograms (CVs) were recorded on a Princeton Applied Research model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/AgCl (0.1 M in acetonitrile), respectively. Potentials were reported with reference to ferrocenium/ferrocene couple  $(Cp_2Fe^{+/0})$ . The magnetization measurements were carried out using a Quantum Design vibrating sample magnetometer (VSM, LakeShore 7037/9509-P) at fields ranging from -9 to 9 kOe at room temperature.

**Monomer Synthesis.** The synthetic routes to ferrocenylbearing monomers 1 and 2(m) (m = 5, 10) are shown in Scheme 1. The detailed procedures are given in the Supporting Information.

**Polymer Synthesis.** All the polymerization reactions and manipulations were carried out under a nitrogen atmosphere using Schlenk techniques in a vacuum-line system except for the purification of the resulting polymers, which was done in an open atmosphere. The synthetic routes of P1 and P2(m) are shown in Scheme 2. Typical experimental procedures are given in the Supporting Information.

**Polymer/CNT Hybridization.** Taking the preparation of P1/ MWNT hybrid for example, into a tube were added 10 mg of P1, 5 mg of MWNTs, and 3 mL of THF. After sonication for 15 min (or vigorous stirring for 1 h), the mixture was filtered through a disposable glass Pasteur pipet filled with absorbent cotton to remove insoluble MWNTs. The filter was dried in vacuo at 100 °C to a constant weight. The concentration of MWNTs in THF (*c*) was calculated by eq 1:

$$c = \frac{W_{\rm CNT} - (W_{\rm F} - W_{\rm F,0})}{V_{\rm S}} \tag{1}$$

where  $W_{\text{CNT}}$  is the original weight of the MWNTs,  $W_{\text{F}}$  and  $W_{\text{F},0}$ are the weights of the cotton filter after and before filtration, respectively, and  $V_{\text{S}}$  is the volume of the solvent. ( $W_{\text{F}} - W_{\text{F},0}$ ) is thus the weight of the insoluble MWNTs retained by the filter, and  $W_{\text{CNT}} - (W_{\text{F}} - W_{\text{F},0})$  is the weight of the soluble MWNTs that passed through the filter. To learn the effect of the ferrocenecontaining PPAs on the solubilization of CNTs, the content of CNTs in the CNT/polymer hybrid (c', %) was calculated by eq 2:

$$c' = \frac{W_{\rm CNT} - (W_{\rm F} - W_{\rm F,0})}{W_{\rm P} + W_{\rm CNT} - (W_{\rm F} - W_{\rm F,0})} \times 100$$
(2)

where  $W_P$  is the weight of the polymer added into the solution.

#### **Results and Discussion**

**Polymer Syntheses.** As shown in Scheme 1, ferrocenecontaining monomers 1 (M1) and 2(m) (m = 5, 10) were synthesized by two-step esterification reactions. Each reaction went smoothly, and desired monomers were obtained in high yields ( $\sim 83-87\%$ ). To transform the monomers to polymers, we tried to use three catalysts based on rhodium (I), which are

 TABLE 1: Polymerization of Ferrocene-Containing

 Acetylene Monomers<sup>a</sup>

			yield								
no.	catalyst	solvent	(%)	$M_{ m w}{}^b$	$M_{\rm w}/M_{\rm n}{}^b$						
1											
1	$[Rh(cod)Cl]_2^c$	DCM/Et <sub>3</sub> N	96.0	242 200	3.0						
2	[Rh(cod)Cl] <sub>2</sub>	THF/Et <sub>3</sub> N	96.3	182 500	3.3						
3	$[Rh(nbd)Cl]_2^c$	DCM/Et <sub>3</sub> N	97.8	193 200	3.5						
4	[Rh(nbd)Cl]2	THF/Et <sub>3</sub> N	99.6	646 800	3.5						
$5^d$	Rh <sup>+</sup> (nbd)	THF	98.1	391 500	4.1						
	$[C_6H_5B^-(C_6H_5)_3]^c$										
<b>2</b> (5)											
6	[Rh(cod)Cl]2	DCM/Et <sub>3</sub> N	24.7	42 600	1.5						
7	[Rh(nbd)Cl] <sub>2</sub>	DCM/Et <sub>3</sub> N	22.5	29 200	1.4						
8	[Rh(nbd)Cl] <sub>2</sub>	THF/Et <sub>3</sub> N	45.6	69 600	1.9						
$9^d$	Rh <sup>+</sup> (nbd)	THF	30.8	87 500	5.7						
	$[C_6H_5B^-(C_6H_5)_3]$										
<b>2</b> (10)											
10	$[Rh(cod)Cl]_2$	DCM/Et <sub>3</sub> N	23.3	60 000	1.7						
11	[Rh(nbd)Cl]2	DCM/Et <sub>3</sub> N	26.6	27 700	2.0						
12	[Rh(nbd)Cl] <sub>2</sub>	THF/Et <sub>3</sub> N	40.6	96 300	2.1						
$13^{d}$	Rh <sup>+</sup> (nbd)	THF	20.8	42 100	4.4						
	$[C_6H_5B^-(C_6H_5)_3]$										

<sup>*a*</sup> Carried out under nitrogen at room temperature for 24 h.  $[M]_0$ = 0.2 M, [cat.] = 2 mM. <sup>*b*</sup> Determined by GPC in THF on the basis of a polystyrene calibration. <sup>*c*</sup> Abbreviations: cod = 1,5-cyclooctadiene; nbd = 2.5-norborndiene. The structures of the catalysts are shown in the Supporting Information. <sup>*d*</sup> Carried out at 60 °C.

known to work as effective catalysts for the polymerizations of monosubstituted acetylenes.

To polymerize the monomers, organorhodium complexes [Rh(diene)Cl]<sub>2</sub> and a zwitterionic catalyst Rh<sup>+</sup>(nbd)- $[C_6H_5B^-(C_6H_5)_3]$  were used. The polymerization results are listed in Table 1. For M1, in DCM/Et<sub>3</sub>N or THF/Et<sub>3</sub>N, both [Rh(cod)Cl]<sub>2</sub> and [Rh(nbd)Cl]<sub>2</sub> are efficiently enough to initiate the polymerization. In each case, polymeric product was obtained in high yield (in the case of no. 4, up to 99.6%) with high molecular weight ( $M_w$  up to 646 800). When the zwitterionic catalyst was chosen, the polymerization was carried out in pure THF, and the result was also quite satisfactory, with  $M_{\rm w}$  being as high as 391 500 at a yield of 98.1%. For M2(5) and M2(10), under the same conditions as M1, it seems that the catalysts also worked well; however, the molecular weights and yields were obviously lower than those of P1. The lowered yields of P2(5) and P2(10) should be ascribed to the formation of some low molecular weight polymers during the polymerization. Generally speaking, these polymers with low molecular weights were stably suspended in methanol, and were not sufficiently collected in the resulting products. This is also why P2(5) and P2(10) showed relatively narrow molecular distributions.

**Structure Characterization.** The polymeric products were characterized by spectroscopic methods. All the polymers gave satisfactory analysis data corresponding to their expected molecular structures (see Supporting Information for details). An example of the IR spectrum of P1 is shown in Figure 1; the spectrum of its monomer M1 is also given in the same figure for comparison. The monomer exhibits three characteristic absorption bands at 3253, 2107, and 1708 cm<sup>-1</sup>, which are assigned to the stretching vibrations of =CH, C=C and C=O, respectively. The first two bands associated with acetylenic absorptions completely disappear in the spectrum of P1, while that of C=O keeps intact, indicating that the triple bond of M1 has been fully consumed by the polymerization reaction.



Figure 1. IR spectra of (A) monomer M1 and (B) its corresponding polymer P1.



Figure 2. <sup>1</sup>H NMR spectra of (A) monomer M1 and (B) its polymer P1 in chloroform-d at room temperature. The solvent peaks are marked with asterisks.

NMR spectroscopy provides valuable information about the structure of the polymers. As can be seen from the <sup>1</sup>H NMR spectrum of P1, no resonance peak can be found at  $\delta$  3.2, which is associated with the acetylene proton (Figure 2B). Meanwhile, a new peak due to the resonances of olefinic protons appears at  $\delta$  5.7, which is absent in the spectrum of its monomer M1. It suggests that the polymerization reaction successfully transforms the acetylenic triple bond of M1 to an olefinic double bond of polyene. This also upfield-shifts the resonances of the phenyl protons, which now occur at  $\delta$  7.6 and 6.7 (Figure 2B, peaks c and b), while its monomer's peaks exist at  $\delta$  8.0 and 7.5, respectively. Like IR spectra, the <sup>1</sup>H NMR spectra confirm that the triple bond of the monomer has been thoroughly transformed to a double bond during the polymerization process.

Figure 3 shows the <sup>13</sup>C NMR spectra of P1 and M1. Whereas the acetylenic carbon atoms of M1 resonate at  $\delta$  80.5 and 83.1, these peaks are completely absent in the spectrum of P1. Instead, two new peaks are observed at  $\delta$  139.0 and 145.9, which are assignable to the resonances of the polyene carbons of the polymer. This once again proves that the polymerization is realized through the transformation of the triple bonds of the monomer to the double bonds of the polymer.

**Absorption Spectra.** The absorption spectra of the polymers and M1 are given in Figure 4. As can be seen from the inset, M1 has a wide absorption region and shows a peak at around 445 nm, which should be ascribed to the featured absorption of ferrocene.<sup>29</sup> However, the absorption of M1 is very weak beyond 300 nm. In contrast, all the polymers have moderate absorbance at  $\sim$ 300 nm and well extend to >500 nm. The enhanced



Figure 3. <sup>13</sup>C NMR spectra of (A) monomer M1 and (B) its polymer P1 in chloroform-d at room temperature. The solvent peaks are marked with asterisks.



**Figure 4.** Absorption spectra of M1, P1, P2(5), and P2(10) in THF at room temperature. Concentration =  $1 \times 10^{-4}$  M. The inset is the magnified curve for M1 in the range of 300–600 nm.

intensities should be due to the polymer main chains whose absorptions are overlapped with the characteristic absorption of ferrocene pendants. Such a wide absorption region is also reasonable when taking into account that conjugated polymers generally possess segments with different lengths of electronic conjugation. Another thing that should be pointed out is the difference of the absorptions between P1 and P2 (*m*) (m = 5, 10): P1 has a much higher and wider absorption beyond 360 nm when compared with that of the other two polymers. This could be ascribed to the effect of the carbonyl group (C=O), which extends the effective conjugation length of P1. Meanwhile, C=O is also an auxochrome group, which is helpful to enhance the absorption of the polymer.

**Polymer/CNT Hybridization.** Hybrids of ferrocene-based compounds and CNTs have potential applications in photovoltaic devices due to the effective electron transfer between them. However, to date, only a few works have focused on ferrocene or its derivative functionalized CNTs.<sup>15,30</sup> Herein, we tried to use ferrocene-containing PPAs to fabricate conjugated polymer/ CNT hybrid nanomaterials. Since PPA main chains can wrap CNTs via physical adsorption,<sup>18a</sup> and ferrocene pendants can also interact with CNTs through  $\pi - \pi$  interactions,<sup>30</sup> it is expected that ferrocene-containing PPAs/CNT hybrids with high



**Figure 5.** TEM (A,B) and SEM (C,D) images of MWNTs encapsulated by P1. The scale bars in both C and D are 1  $\mu$ m.

solubilities in common organic solvents and high loading amount of CNTs can be obtained. Fortunately, as expected, both SWNTs and MWNTs wrapped by P1 were highly soluble in common solvents, such as DCM, THF, DMSO, and CHCl<sub>3</sub>. For example, as shown in Figure S1, P1/SWNT and P1/MWNT dispersed well in THF to form homogeneous black solutions. The hybrid solutions were stable and could stand for months without precipitation. Additionally, their dried powders could be redispersed in common organic solvents.

Morphologies of the Hybrids. Direct observation of the morphology of the hybrids is not only a powerful technique to study the microstructure of the composites, but also a direct method to illuminate the interactions between different components. Morphological images of P1-functionalized CNTs are shown in Figure 5 and Figure S2 (see Supporting Information for details). From the TEM images (Figure 5A,B), it is clear that the MWNTs have been wrapped by thick polymer shells. The SWNTs were also densely wrapped by P1, as can be seen in Figures S2(A) and S2(B). The strong association between CNTs and polymer chains leads to the high solubility of the hybrid nanomaterials in organic solvents. The SEM images (Figure 5C,D) of P1/MWNT hybrid nanomaterials show that the MWNTs are embedded in the polymer matrix, and the MWNTs are uniformly dispersed. Both TEM and SEM measurements imply that, with the assistance of P1, the CNTs were separated from their bundles, and enjoyed a good dispersity in organic media. The thick wrapping of the polymer chains onto CNTs and the good dispersity of the hybrids in the polymer matrix provide a chance to study the properties of onedimensional functional materials. In addition, it endows the composite with integrated merits of the ferrocene-containing PPAs and CNTs. The electron donor/acceptor (ferrocene and polymer main chain/CNTs) assembly not only has a potential application in photovoltaic devices, but is also suitable to apply in sensors, electrodes, and so on.3,15,24-26

High-resolution transmission electron microscopy (HRTEM) of the hybrids and TEM images at higher magnifications are displayed in Figure 6. In Figure 6A,B, the lattices of SWNTs and MWNTs are clearly shown. Figure 6C exhibits the TEM image of P1/MWNT in a much larger area, and the polymer shell and MWNT core can easily be distinguished. However, when the hybrid was filtrated and washed through a filter membrane with a pore-size of  $0.22 \,\mu$ m, it is observed that not only free polymers but also some of the polymers attached to MWNTs were removed from the hybrids. As shown in Figure



**Figure 6.** HRTEM for (A) P1/SWNT, (B) P1/MWNT, and (C,D) larger area TEM images for P1/MWNT. In panel C, the sample was directly used without removing free polymers, and in panel D, the samples were filtered and washed through a micropore filter membrane (pore size  $\sim$  0.22  $\mu$ m).



Figure 7. Solubilities of M1-, P1-, and PPA-functionalized SWNTs and MWNTs in THF.

6D, no obvious polymer shells can be observed on the surfaces of MWNTs. However, they still can be redispersed in organic solvents, and the suspension can stand for hours, even to 1 day. The difference in stabilities between the samples is evidence of the positive effect of the polymers in the hybrids. And their image contrast confirms the inherent physical adsorption feature of noncovalent functionalization of CNTs.

**Polymer Effect on Solvating Power.** Solvating power of the compound in dispersing CNTs is an important parameter for fabricating soluble hybrids. To quantitatively evaluate the solvating powers of the polymers (P1 and PPA) and M1, we measured the solubilities of CNTs in THF by using eq 1. All the measurements were carried out in identical conditions to ensure the data can be compared with each other. The experimental results are displayed in Figure 7. The data revealed that, with the aid of P1, the solubilities of SWNTs and MWNTs in THF are as high as 633 and 967 mg/L, respectively. The high performance should be ascribed to the "additive effect" of the PPA skeleton and ferrocene pendants.

More important, we found it is quite a positive "additive effect"; that is to say, an enhanced "synergistic effect" was

CHART 1



observed. As can be seen from the photographs in Figure S1, both M1 and P1 can help dissolve CNTs in THF, giving homogeneous hybrids solutions. However, it is not difficult to find out the difference between M1- and P1-functionalized CNTs solutions from the evident contrast of their colors. For M1/CNT hybrids, the solutions are light, whereas those of P1/CNTs are dark colored. The photographs indicate that much more CNTs are involved in the P1/CNT hybrids than in the M1/CNTs. This is confirmed by the solubility data presented in Figure 7. Under the same conditions, M1-modified CNTs showed much lower solubility in THF, only 167 and 133 mg/L for SWNTs and MWNTs, respectively. This observation suggests that there may be a profound "polymer effect" on the solvating power, and this effect may be related to the polymers' PPA skeletons, which can effectively wrap on CNTs through  $\pi - \pi$  interactions. To illuminate the effect of PPA skeleton, the solubilities of PPAfunctionalized SWNTs and MWNTs were checked by the physical blending of PPA with SWNTs and MWNTs in THF. Under the same molar concentration as that of P1, it is found that the solvating power of PPA is much less than that of P1, only 133 and 100 mg/L for SWNTs and MWNTs in THF, respectively. In contrast, the solubilities of P1-modified SWNTs and MWNTs in THF are as high as 633 and 967 mg/L, respectively. It means that P1 has much higher solvating powers than the sum of those for PPA and M1. The greatly enhanced solubilities of CNTs in THF after "conjugation" with P1 is evidence of the "synergistic effect" between PPA skeleton and ferrocene pendants.

Mechanism of CNT Solubilization. On the basis of the above results, the solubilization of CNTs may be realized through the following mechanisms: For M1, the molecules are attracted to the CNT shells because of the electronic interactions between ferrocene motifs and the CNT surfaces; for PPA, the polymer chains can wrap onto the CNT surfaces through  $\pi - \pi$ interactions between the phenyls and CNTs; for P1, both PPA skeletons and ferrocene pendants take effects, and the affinity of the polymer chains with the solvent molecules brings the polymer-wrapped CNTs into the liquid media, leading to the dissolution of CNTs in the organic solvents. Additionally, the polymer chains attached to CNT surfaces may attract other polymer chains via pendant-pendant electronic interaction, resulting in a thick coating of polymer chains around the CNT shells. Two factors, i.e., polymer wrapping and the  $\pi - \pi$ interactions between CNTs and ferrocene pendants, are considered to play important roles in dissolving CNTs in solvents. A schematic illustration is shown in Chart 1.

Film Forming Ability of the Nanohybrid. A unique advantage of the polymer-based materials over small molecules and inorganic materials is their solution processability and good film formability. Thanks to their good solubilities in organic solvents, P1/CNT hybrids are expected to show good film



Figure 8. Photographs of (A) P1/SWNT powder and its corresponding film cast on quartz substrate, and (B) transparent hybrid film of P1/SWNTs.



**Figure 9.** Optical-limiting response of THF solutions of P1, P1/MWNT hybrid, and toluene solution of  $C_{60}$  to 8-ns, 10 Hz pulses of 532-nm laser light. Light path length: 1 mm. The hybrid was prepared according to the above manipulations.

formability. To check this point, we took P1/SWNT hybrid as a model to conduct the film fabrication. As expected, when a solution of P1/SWNT in chloroform was cast onto quartz substrate, a thin film was formed after a mild evaporation at room temperature. As displayed in Figure 8, the pristine hybrid is a black—brown powder, and its cast thin film is uniform and transparent, which indicated good dispersion of CNTs in polymer matrix and desirable film forming ability of the hybrid. This intrinsic property makes the hybrids easy to be processed into high-quality films with tunable shape and thickness. The good solubilities, good film forming abilities, and long-term stabilities pave the way for the applications of ferrocenecontaining PPAs/CNTs hybrids.

Optical-Limiting Property. The optical-limiting behaviors of the THF solutions of P1 and P1/MWNT hybrid were investigated by employing the experimental setup used in our previous studies.<sup>31</sup> For comparison, the optical-limiting behavior of C<sub>60</sub> in toluene was also studied. In order to compare the optical-limiting powers among them, their transmittances were set to the same level by concentration adjustments. As shown in Figure 9, their transmittances were set at 0.9 in the linear region. When the THF solution of P1 was shot by 8-ns pulses of 532-nm laser light, the transmitted fluence linearly increased with the increase of the input fluence. This polymer, like many other polyacetylenes, is thus nonlinear optically inactive. It is reasonable that there are no bulky effective conjugated systems in P1. Even though its main chain is conjugated and ferrocene units are usually used to construct optical-limiting active materials, the effective conjugation length is short, and ferrocene pendants are isolated from the conjugated centers without forming an expanded conjugated system. However, when



**Figure 10.** CVs of ferrocene-containing polymers and the hybrid in DCM containing 0.5 M [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub>. Scan rate: 100 mV/s. Concentration (mM): P1: 7.7; P2(5): 5.0; P2(*10*): 4.6; P1/MWNT: 7.7 for P1.

MWNTs are incorporated, the hybrid of P1/MWNT acts in quite a different way; it exhibits an optical-limiting property at high input flow capacity. As shown in Figure 9, its optical-limiting power is evidently higher than  $C_{60}$ . For example, at incident fluence of 976 mJ/cm<sup>2</sup>, the transmitted fluence for  $C_{60}$  is 797 mJ/cm<sup>2</sup>, while, for P1/MWNTs, the transmitted fluence is only 739 mJ/cm<sup>2</sup> at the identical incident fluence. In consideration that  $C_{60}$  is a famous optical-limiting material, the hybrids of ferrocene-containing PPA derivatives and MWNTs are promising optical-limiting materials.

Electrochemical Property. Ferrocene is a representative redox active compound.<sup>24-26</sup> Thus, the resulting polymers and the hybrids are also envisioned as being electrochemically active. To check this idea, the reversibility and oxidation potentials of the redox processes of the polymers and P1/MWNT hybrid were characterized by CV in DCM solutions. Figure 10 shows the CVs of the polymers and the hybrid. The oxidation potential of P1, P2(5), P2(10), and P1/MWNT are summarized in Table 2. The CV curves and the extracted data offer the following information. First, it is found that all the samples exhibit only one single wave in the range from -0.3 to 1.2 V (vs Ag/AgCl), which is assigned to the oxidation of the ferrocene motifs, implying that the electrochemical activity of the conjugated polyene backbone is undetectable under our measurement conditions. Second, different polymers, i.e., P1, P2(5), and P2(10) display similar electrochemical behavior in DCM. These results indicate the absence of direct interactions between the iron centers, just as observed for many ferrocene-containing dendrimers and side-chain polyferrocenes.<sup>32</sup> Meanwhile, these results also suggest the lack of electronic coupling between the ferrocene motifs and the conjugated polyene backbones. When the data of P1 were compared with that of P1/MWNT hybrid, it was found that the  $E_{pc}$  of P1/MWNT is higher than that of P1 by 38 mV, while the  $E_{pa}$  of P1/MWNT is lower than that of P1 by 19 mV. It suggests that the P1/MWNT hybrid mainly keeps the redox property of ferrocenyl pendants. Nevertheless, the small but detectable increase in the oxidation potential may be ascribed to the electronic interactions between MWNTs and ferrocene pendants of the conjugated polymer chains. Because of the electronic interaction between them, electrons can be transferred from the ferrocene donors to the MWNTs acceptors.

**Thermal Stability and Pyrolytic Ceramization.** The thermogravimetric analysis results of the polymers and the P1/MWNT hybrid are shown in Figure 11. It is found that the  $T_d$ 

(the temperature at which the sample loses 5% of its weight) for P1, P2(5), P2(10), and P1/MWNTs is 342, 320, 330, and 346 °C, respectively. These are much higher than that of PPA, whose  $T_d$  is only 225 °C.<sup>33</sup> The thermal analysis results suggest that the ferrocene pendants can improve the thermal stability of the PPA derivatives. This effect should be ascribed to the "jacket effect" of the ferrocene pendants surrounding the polyene backbone.<sup>18b,22,23</sup>

It is worth noting that, during the course of temperature increasing, two platforms are observed on the TGA curves. Before 340 °C, the polymers lost little of their weights; however, sharp decreases of weight were found between 340 to  $\sim$ 400 °C, and then leveled off when heated to about 487 °C. The second platform occurred between ~490-610 °C, and little weight loss was recorded during this temperature region, indicating that the polymers had been ceramized in the pyrolysis process. Further weight loss of the polymers was found when heating the samples to much higher temperatures, as shown in Figure 11. The ceramic yields of the polymers at 500 and 900 °C are summarized in Table 2. The data at 500 °C for P1, P2(5), and P2(10) are 52.8%, 42.6% and 31.6%, respectively. It is reasonable, when we take into account the structure differences between the polymers, that the polymers with lower content of alky spacers should have higher ceramic yields. It seems that the pyrolytic behaviors became complicated at higher temperatures. When the temperature reached 900 °C, the ceramic yield of P2(10) was even higher than that of P2(5). The pyrolytic behavior of P1/MWNT hybrid is also shown in Figure 11; it acted in a way similar to P1. Nevertheless, because of the incorporation of MWNTs, the hybrid showed higher transition temperatures than those of P1.

Compositions and Morphologies Study. As reported elsewhere, linear or hyper-branched ferrocene-containing polymers can be utilized as precursors to magnetic ceramics.<sup>34</sup> Thus we checked whether our ceramics were magnetic by attaching a piece of magnet to the resulting products of TGA tests. It is found that all of the resulting powders could be attracted to the magnet, evidencing that the products are really magnetic. To further explore the magnetic properties of ceramics, we newly prepared the ceramics by putting P1 and P1/MWNTs into an argon-filled furnace at 1000 °C for 1 h. The ceramic yields for P1 and P1/MWNTs are 30.9% and 44.3%, respectively. X-ray diffraction (XRD) measurements were conducted on the ceramic products. Figure 12 shows the XRD patterns of the ceramics obtained from pure P1 and P1/MWNTs hybrid. In comparison with the pattern of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> standard, the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in both samples was clearly confirmed. Therefore, it is unambiguous that the magnetism of the ceramics is due to the existence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in the resulting products.

We also used XPS and EDX techniques to analyze the ceramic products in order to learn their chemical compositions. As shown in Figure 13, both the ceramics prepared from P1 and P1/MWNT are composed of iron (Fe), oxygen (O), and carbon (C) species. The EDX analyses presented in Figure 14C and 14F further confirm the existence of Fe element as revealed by XPS data. The SEM images of ceramics from P1 and P1/MWNT in the furnace at 1000 °C under argon are given in Figure 14A,B and Figure 14D,E. As shown in Figure 14 A, though most of the ceramic particles from P1 are attached together to form bulky aggregates, some particles with diameters of around several hundred nanometers still remain isolated on the surface. For the hybrid product, the ceramic forms in bulk matrix, and the CNTs are well dispersed in it. The SEM images for ceramic obtained from P1/MWNT hybrid thus further

TABLE 2: Thermal and Electrochemical Properties of the Polymers and Hybrids

sample	$T_{\rm d}$ (°C) <sup>a</sup>	ceramic yield (500 °C, %) <sup>b</sup>	ceramic yield (900 °C, %) <sup>b</sup>	$E_{\rm pc}~({\rm V})^c$	$E_{\rm pa}~({\rm V})^c$	$E_{1/2} (\mathbf{V})^d$	$\Delta E_{\rm p}~({\rm mV})^e$
P1	342	52.8	34.1	0.556	0.651	0.604	95
P <b>2</b> (5)	320	42.6	8.3	0.546	0.633	0.588	87
P <b>2</b> (10)	330	31.6	16.0	0.540	0.635	0.588	95
P1/MWNT	346	57.1	47.5	0.594	0.632	0.613	38

<sup>*a*</sup> Temperature for 5% weight loss determined by TGA under nitrogen. <sup>*b*</sup> Obtained from TGA results. <sup>*c*</sup> Determined by CV analysis, where  $E_{pa}$  is the potential of the anodic peak current and  $E_{pc}$  is the potential of the cathodic current. <sup>*d*</sup> Formal redox potential  $E_{1/2} = (E_{pa} + E_{pc})/2$ . <sup>*e*</sup>  $\Delta E_{p} = E_{pa} - E_{pc}$ .



**Figure 11.** TGA thermograms of P1, P2(*10*), P2(*10*), MWNTs, and P1/MWNTs under nitrogen at a heating rate of 10 °C/min.



**Figure 12.** XRD patterns of the ceramics obtained from P1 and P1/ MWNTs. The vertical lines are the reference data for the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> standard taken from the Power Diffraction File 39-1346, International Centre for Diffraction Data (ICDD).

confirm the uniform dispersion of the functionalized CNTs in polymer matrix.

**Magnetic Property.** As mentioned above, the ceramic particles are magnetic and can be attracted by a magnet bar. Thus we used a Quantum Design VSM to investigate their magnetization behaviors in externally applied magnetic field with a field strength ranging from -9 to 9 kOe. The magnetization as a function of magnetic field strength is shown in Figure 15. For both ceramic samples derived from P1 and P1/MWNT hybrid, the magnetization rapidly increased with the increase of the field strength and became leveled off at  $\sim$ 8.8 or -8.8 kOe. These behaviors indicate that they are superparamagnetic materials. For both of the samples, hysteresis behaviors are observed. For the ceramic generated from P1 (curve a), only



Figure 13. XPS spectra of (a) ceramic product from P1 and (b) ceramic product from P1/MWNT hybrid under argon at 1000  $^{\circ}$ C for 1 h.

very small hysteresis loop with a coercive force  $(H_c)$  of 32 Oe is recorded. However, for the ceramic obtained from P1/MWNT hybrid (curve b), a much more obvious hysteresis loop can be observed, and a coercive force of 304 Oe was recorded. Another characteristic observed in Figure 15 is the difference in saturation magnetization  $(M_s)$  between the two samples. The  $M_{\rm s}$  values of the ceramics derived from P1 and P1/MWNT hybrid are 29.9 and 26.9 emu/g, respectively. At first sight, it seems that the ceramic from P1 has a higher  $M_s$  than that from the hybrid product. In fact, the difference may be largely ascribed to the relative content of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in these two samples. In the case of P1/MWNTs hybrid, the component of MWNTs should also be taken into account. The weight content of MWNTs in original P1/MWNTs hybrid is 22.5% (see Figure 7), and based on the data of TGA analysis and the ceramic yields of P1 and P1/MWNTs, after pyrolysis, there is no less than 18.0% MWNTs pyrolytic product in the resulting powders. Since MWNTs component has no contribution to the magnetization at all, the net  $M_s$  rendered from the component of P1 in P1/MWNT hybrid is about 32.8 emu/g, which is over 9.7% higher than that of P1. Even taking the residual iron catalyst embedded in the MWNTs into account, because of the trace amount, it still can not give rise to such an evident increase. Yet, the origin of this magnetization increase has not been elucidated and needs further investigation.

#### Conclusions

Ferrocene-containing PPAs have been synthesized by using organorhodium complexes  $[Rh(diene)Cl]_2$  and  $Rh^+(nbd)$ - $[C_6H_5B^-(C_6H_5)_3]$  as catalysts. Their structures have been thoroughly characterized by a combination of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and UV techniques. Attachment of ferrocene pendants onto PPA backbone conferred a few noticeable properties on the resultant polymers. First, the polymers (P1, P2(5), and



Figure 14. (A,B and D,E) SEM graphs of ceramic products from P1 and P1/MWNT hybrid under argon at 1000 °C for 1 h, respectively; (C,F) EDX spectrum of ceramic products from P1 and P1/MWNT hybrid, respectively.



Figure 15. Magnetization curves for the ceramic products obtained from (a) P1 and (b) P1/MWNT hybrid at room temperature ( $\sim$ 25 °C).

P2(10)) can efficiently wrap around both SWNTs and MWNTs to generate hybrids, which are highly soluble in common organic solvents. The solubilities of P1-functionalized SWNTs and MWNTs in THF are up to 633 and 967 mg/L, respectively. In comparison with M1, P1 showed a profound "polymer effect". Additionally, the solvating powers of P1 are much higher than the sum of those for PPA and M1. We ascribed the high solvating powers to the "synergistic effect" of the PPA skeleton and ferrocene pendants.

The second merit of P1/MWNT is its noticeable opticallimiting property. At high incident laser fluence, the opticallimiting power of P1/MWNT is higher than that of C<sub>60</sub>, which is considered as a representative optical-limiting material. Third, the CV measurement results demonstrated that the polymers and the hybrids inherited the unique redox activity of ferrocene pedants. The  $\pi$ - $\pi$  interactions between CNTs and ferrocene motifs induced the significant wrapping of polymer chains onto CNTs. Therefore, the loading of CNTs into soluble ferrocenecontaining PPAs provides a route to immobilization of multiple redox active centers on tractable one-dimensional CNTs.

Finally, after pyrolysis, the polymers and hybrids were changed into ceramics. All these ceramic samples are superparamagnetic materials as revealed by the measurement results on a Quantum Design VSM. The saturation magnetization ( $M_s$ ) of the ceramics derived from P1 and P1/MWNT hybrid is 29.9 and 26.9 emu/g, respectively. The latter datum is in the list of the best results reported for the magnetic nanocomposites obtained by the attachment of magnetic nanoparticles onto CNTs.<sup>35</sup> With a combination of excellent solubility, good film formability, and improved stability of the hybrids, our approach offers a versatile route to large-area, redox-active substrates, optical-limiting matrices, and magnetic films, which may find an array of high-tech applications.

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**Supporting Information Available:** Figures showing supplementary TEM and SEM images for the P1/SWNT hybrid and absorption and emission spectra of P1, CNTs, and their hybrids in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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