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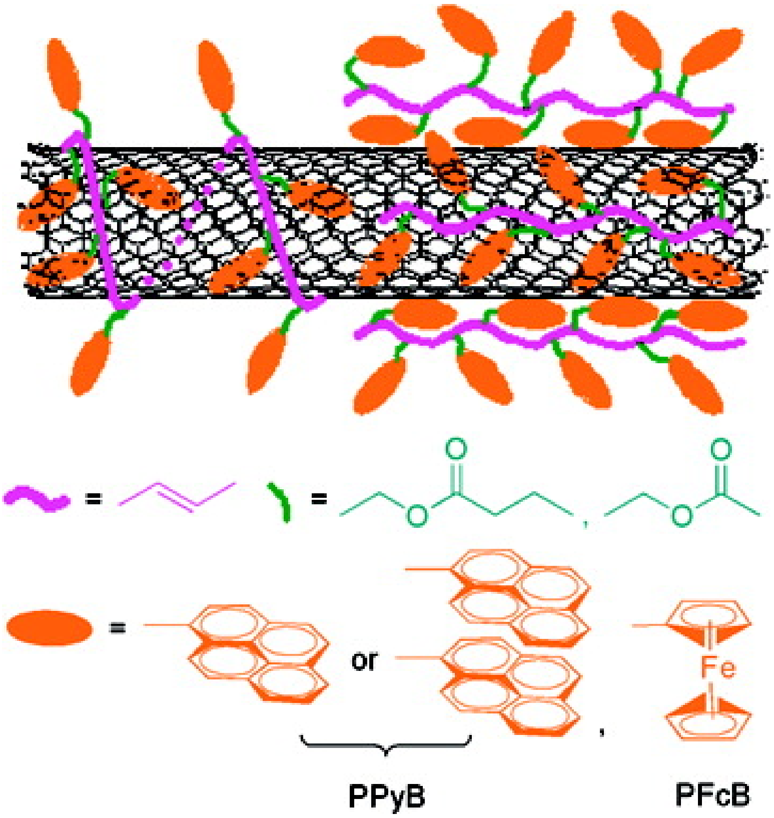

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Electronic Interactions and Polymer Effect in the Functionalization and Solvation of Carbon Nanotubes by Pyrene- and Ferrocene-Containing Poly(1-alkyne)s

Wang Zhang Yuan,[†] Yu Mao,[†] Hui Zhao,[†] Jing Zhi Sun,*[,†] Hai Peng Xu,[†] Jia Ke Jin,[†] Qiang Zheng,[†] and Ben Zhong Tang*[,†,‡]

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ABSTRACT: 4-[3-(1-Pyrenyl)propylcarbonyloxy]-1-butyne (PyB) and 4-ferrocenylcarbonyloxy-1-butyne (FcB) were effectively polymerized by zwitterionic rhodium complex $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$, giving corresponding polymers PPyB and PFcB with high molecular weights (M_w up to 33300) in high yields (up to 83%). The polymers are excellent solvating agents in making carbon nanotubes (CNTs) soluble in common organic solvents. The salvation is aided by the wrapping or coating of CNTs by the polymers through strong electronic interactions between the aromatic pendants and the CNT shells. A pronounced "polymer effect" was observed in the solvating process: the polymers showed much higher solvating power than their monomers. The polymers endowed the CNTs with functional properties: the PPyB/CNT and PFcB/CNT hybrids were light-emitting and redox-active, respectively.

Introduction

The remarkable mechanical, thermal, and electrical properties of carbon nanotubes (CNTs) make them promising candidate materials for a wide range of technological applications.[1−5] Realization of the application potential has, however, been hampered by the notorious intractability of CNTs. The strong hydrophobicity, $\pi-\pi$ stacking and van der Waals attraction promote agglomeration of CNTs, rendering them totally immiscible with organic media.[6,7] Much effort has been made to disperse CNTs in common solvents.[8−13] Noncovalent functionalization by conjugated polymers is an intriguing approach, for it may confer desired solubility and new functionality on CNTs without deteriorating their own unique properties.

Polyacetylene is a well-known conjugated polymer.[14] Its derivatives (or substituted polyacetylenes) have attracted much attention due to their novel properties and potential applications.[15−17] The polymers have been found to show photoconductivity, optical nonlinearity, magnetic susceptibility, photo- and electroluminescence, photonic patternability, liquid crystallinity, biocompatibility, cytophilicity, chain helicity, and so on.[15−26] We have been interested in the fabrication of polyacetylene/CNT hybrids.[8c,9a,9b] In our previous work, we solvated CNTs through their noncovalent functionalization by poly(phenylacetylene) (PPA) and its derivatives. In this work, we investigated the functionalization and solvation of CNTs by another group of substituted polyacetylenes, poly(1-alkyne)s.

We designed and synthesized two 1-butyne derivatives containing pyrenyl (PyB) and ferrocenyl (FcB) groups (Scheme 1). While 1-alkyne derivatives have been difficult to polymerize by "traditional" organorhodium catalysts,[17] we succeeded in polymerizing the PyB and FcB monomers by a zwitterionic rhodium complex of $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$. The resultant polymers PPyB and PFcB were much better dispersants than their corresponding monomers, showing a pronounced "polymer effect" in the solvation process. Poly(6-chloro-1-hexyne) (PClH), a poly(1-alkyne) carrying no aromatic pendants (Scheme 2), could not help the dissolution of CNTs, indicating that the strong electronic interactions of the aromatic pendants in PPyB and PFcB with the CNT shells have played an important role in the functionalization and solvation processes.

Experimental Section

General Information. Tetrahydrofuran (THF) and 1,4-dioxane were distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use. Dichloromethane (DCM) and toluene were distilled from calcium hydride under argon. *N*,*N′*-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and *p*-toluenesulfonic acid monohydrate (TsOH) were purchased from Aldrich and used as received. 1-Pyrenebutyric acid and ferrocenecarboxylic acid were purchased from Alfa Aesar and Yixing Weite Petrochemical Additives, respectively. Rhodium complexes $[Rh(nbd)Cl]_2$ (nbd = norbonadiene), $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), and $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$ were prepared according to published procedures.[27,28] Single-walled carbon nanotubes (SWNTs) were purchased from Strem, and multiwalled carbon nanotubes (MWNTs) were prepared by a chemical vapor deposition process.

^1H and ^{13}C NMR spectra were measured on a Bruker ARX 500 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. IR spectra were recorded on a Bruker VECTOR 22 spectrometer. UV−vis absorption spectra were measured on a Varian CARY 100 Bio spectrophotometer. 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 in THF by a Waters associated gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering molecular weight range of 10^3-10^7 was used for molecular weight calibration. Raman spectra were measured on a Jobin Yvon Raman spectrometer at a laser excitation

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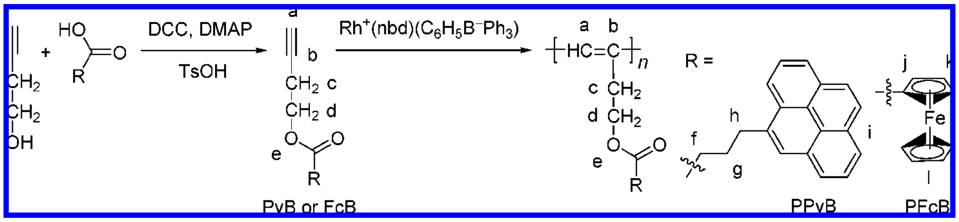
Scheme 1



Scheme 2

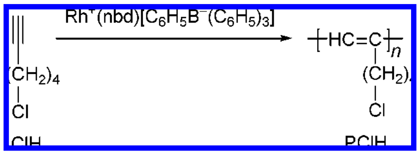


Table 1. Polymerizations of Pyrene- and Ferrocene-Containing 1-Butynes[a]

no.	catalyst[b]	solvent	yield (%)	M_w[c]	M_w/M_n[c]
		PyB Monomer			
1	$[Rh(cod)Cl]_2$	THF/Et_3N	7.2	1700	1.1
2	$[Rh(cod)Cl]_2$	DCM/Et_3N	25.6	9300	3.9
3	$[Rh(nbd)Cl]_2$	THF/Et_3N	26.6	26 200	4.1
4	$[Rh(nbd)Cl]_2$	DCM/Et_3N	70.4	30 200	2.9
5	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	THF	80.5	33 300	1.7
6	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	DCM	76.1	29 900	1.7
7	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	toluene	56.1	24 500	1.6
8	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	1,4-dioxane	38.0	15 000	1.4
		FcB Monomer			
9	$[Rh(cod)Cl]_2$	THF/Et_3N	5.6	1700	1.1
10	$[Rh(cod)Cl]_2$	DCM/Et_3N	13.0	6500	1.5
11	$[Rh(nbd)Cl]_2$	THF/Et_3N	5.7	2600	1.2
12	$[Rh(nbd)Cl]_2$	DCM/Et_3N	33.9	24 300	2.4
13	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	THF	83.2	14 500	1.5
14	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	DCM	76.7	18 600	1.8
15	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	toluene	46.7	9400	1.9
16	$Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$	1,4-dioxane	25.8	8500	1.7

[a] Carried out under nitrogen at 30 °C for 24 h. $[M]_0 = 0.2$ M, [cat.] = 2 mM. [b] Chemical structures of the catalysts are given in Chart S1 (Supporting Information). Abbreviations: cod = 1,5-cyclooctadiene; nbd = norbonadiene. [c] Determined by GPC in THF on the basis of a polystyrene calibration.

wavelength of 325 nm. Transmission electron microscope (TEM) images were recorded with a JEOL/JEM-200 CX TEM at an accelerating voltage of 160 kV. Cyclic voltammograms were recorded on a CHI 600A electrochemical workstation. The tests were carried out in DCM with a Pt anode, using Bu_4NClO_4 as supporting electrolyte. Element analysis was conducted on a Thermo Finnigan Flash EA1112 system.

Monomer Preparation. Monomers PyB and FcB were prepared according to the synthetic route shown in Scheme 1. The detailed experimental procedures and characterization data are given below.

Preparation of 4-[3-(1-Pyrenyl)propylcarbonyloxy]-1-butyne (PyB). Into a 250 mL round-bottom flask were placed 0.35 g (5 mmol) of 4-hydroxy-1-butyne, 1.44 g (5 mmol) of 1-pyrenebutyric acid, 1.55 g (7.5 mmol) of DCC, 122.2 mg (1 mmol) of DMAP, and 190.0 mg (1 mmol) of TsOH in 150 mL of DCM. The resulting mixture was stirred at room temperature for 24 h. After filtering the urea salt formed during the reaction, the solid was washed with diethyl ether, and the filtrate was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using a chloroform/hexane mixture (5:1 by volume) as eluent. A white solid was isolated in 81.3% yield. IR (KBr), ν (cm^{-1}): 3289 (HC≡), 2116 (C≡C), 1739 (C═O). ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 8.2, 8.1, 8.0, 7.9, 7.8 (protons of pyreneyl), 4.1 (m, 2H, $-CH_2OOC$), 3.3 (m, 2H, protons attaching to pyreneyl), 2.5, 2.4 (m, 4H, $\equiv CCH_2$ and $-OOCCH_2$), 2.2 (m, 2H, $-CH_2CH_2$-CH_2), 1.9 (s, 1H, $HC\equiv$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 173.2 (C═O), 135.6, 131.4, 130.8, 129.9, 128.7, 127.4, 126.7, 125.8, 125.0, 124.9, 124.8, 123.2 (carbons of pyreneyl), 80.1 ($C\equiv CH$), 69.9 ($\equiv CH$), 62.0 ($-CH_2OOC$), 33.6, 32.7 ($-OOCCH_2$ and $-CH_2CH_2CH_2$), 26.6 ($-CH_2CH_2CH_2$), 19.0 ($\equiv CCH_2$). Anal. Calcd for PyB: C, 84.68; H, 5.92. Found: C, 84.19; H, 5.94.

Preparation of 4-Ferrocenylcarbonyloxy-1-butyne (FcB). This monomer was synthesized in a similar way to that described above for monomer PyB. A yellow or brown solid was obtained at 85.7% yield. IR (KBr), ν (cm^{-1}): 3295 (HC≡), 2121 (C≡C), 1711 (C═O), 644 (HC≡). ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 4.8, 4.3, 4.1 (9H, protons of ferrocenyl), 4.2 (m, 2H, $-CH_2OOC$), 2.6 (m, 2H, protons which connect to $-CH_2C\equiv CH$), 2.0 (s, 1H, $HC\equiv$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 171.5 ($-C$═O), 80.4 ($C\equiv CH$), 70.7 ($HC\equiv$), 71.4, 70.1, 70.0 (carbons of ferrocenyl), 61.9 ($-CH_2OOC$), 19.2 ($-CH_2C\equiv CH$). Anal. Calcd for FcB: C, 63.86; H, 5.00. Found: C, 63.88; H, 4.98.

Polymer Synthesis. All the polymerization reactions were carried out under nitrogen using Schlenk techniques in a vacuum-line system. Typical experimental procedures for the polymerization of PyB catalyzed by a zwitterionic Rh complex are given below as an example.

Into a 20 mL Schlenk tube with a side arm was added 170 mg (0.5 mmol) of monomer PyB. The tube was evacuated under vacuum and then flushed with dried nitrogen three times through the side arm, after which, 1.5 mL of THF was injected. A catalyst solution was prepared in another Schlenk tube by dissolving 2.5 mg of $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$ in 1 mL of THF. After aging for 15 min, the catalyst solution was transferred to the monomer solution using a hypodermic syringe. The resultant mixture was stirred at 30 °C under nitrogen for 24 h. The mixture was then diluted with 6 mL of THF and added dropwise to 500 mL of hexane through a cotton filter under stirring. The precipitate was allowed to stand for 24 h and then filtered with a Gooch crucible. The polymer was washed with a hexane/acetone mixture (3:1 by volume) five times and dried in a vacuum oven at 40 °C to a constant weight. The polymer was isolated as a gray white solid in 80.5% yield.

Characterization Data of PPyB (Table 1, No. 5). M_w: 33300. M_w/M_n: 1.7. IR (KBr), ν (cm^{-1}): 1731 (C═O). ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.7, 7.6, 7.5, 7.3 (protons of pyreneyl), 5.9 (s, 1H, $-HC$═), 3.9 (2H, $-CH_2OOC$), 2.8 (2H, protons attach to pyreneyl), 2.5 (2H, $-OOCCH_2$), 2.1 (2H, $=CCH_2$), 1.7 ($-CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 172.9 (C═O), 136.0 ($-C$═CH−), 126.6 ($-HC$═), 135.1, 131.0, 130.4, 129.5, 128.3, 126.9, 126.2, 125.3, 124.6, 124.5, 124.3, 122.7 (carbons of pyreneyl), 62.8 ($-CH_2OOC$), 36.9 ($=CCH_2$), 33.4, 32.3 ($OOCCH_2$ and $-CH_2CH_2CH_2$), 26.3 ($-CH_2CH_2$-CH_2). Anal. Calcd for PB−Py: C, 84.68; H, 5.92. Found: C, 84.16; H, 5.94.

Monomer FcB was polymerized in a similar way. Characterization data for PFcB (Table 1, no. 13) are as follows. Yield: 83.2%. M_w: 14500. M_w/M_n: 1.5. IR (KBr), ν (cm^{-1}): 1711 (C═O). ^1H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 6.1 (s, 1H, $-HC$═C−), 4.7, 4.3, 4.1 (m, 11H, protons of ferrocenyl and $-CH_2OOC$), 2.6 (m, 2H, protons connect to $-CH_2C$═CH). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 171.1 ($-C$═O), 136.2 ($-C$═CH−), 129.0 ($-HC$═), 71.4, 70.2, 69.8 (carbons of ferrocenyl), 63.0 ($-CH_2$-OOC), 37.5 ($-CH_2C$═CH−). Anal. Calcd for PB−Fc: C, 63.86; H, 5.00. Found: C, 63.43; H, 4.98.

Polymer/CNT Hybridization. The experimental procedures for the preparation of the composite of PPyB and SWNT are given below as an example. Into a tube were added 7.9 mg (23.3 μmol) of PPyB, 5 mg of SWNT, and 3 mL of THF. After sonication for

15 min, the mixture was filtered through a cotton filter to remove insoluble SWNT. The filter was dried before and after filtration in an oven at 100 °C under vacuum to constant weight. The concentration of SWNT in THF (*c*) was calculated by eq 1[9b]

$$c = \frac{W_{\mathrm{CNT}} - (W_{\mathrm{F}} - W_{\mathrm{F},0})}{V_S} \qquad (1)$$

where W_{CNT} is the original weight of SWNT, W_{F} and $W_{\mathrm{F},0}$ are the weights of the cotton filter after and before filtration, respectively, and V_{s} is the volume of the solvent used. Thus, $(W_{\mathrm{F}} - W_{\mathrm{F},0})$ is the weight of the insoluble SWNT that were retained by the filter, while $W_{\mathrm{CNT}} - (W_{\mathrm{F}} - W_{\mathrm{F},0})$ is the weight of the soluble SWNT that passed through the filter.

Results and Discussion

Polymer Synthesis. As shown in Scheme 1, the pyrene- and ferrocene-containing monomers PyB and FcB were synthesized by the esterifications of 4-hydxoy-1-butyne with 1-pyrenebutyric acid and ferrocenecarboxylic acid, respectively. The reactions proceeded smoothly and the desired monomers were obtained in high yields (>80%).

We first tried to use $[\mathrm{Rh(cod)Cl}]_2$ to polymerize PyB in a THF/$\mathrm{Et_3N}$ mixture. The result was, however, rather disappointing: only was an oligomer obtained in a low yield (Table 1, no. 1). The polymerization carried out in DCM/$\mathrm{Et_3N}$ gave a better result. Even better results were obtained when $[\mathrm{Rh(nbd)Cl}]_2$ was used as catalyst for the alkyne polymerization. Here again, the polymerization in DCM/$\mathrm{Et_3N}$ proceeded better, affording a polymer with an M_{w} value of $\sim 30 \times 10^3$ in a yield of ~70% (Table 1, no. 4).

The zwitterionic complex $\mathrm{Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]}$ was found to be an excellent catalyst for the alkyne polymerization. In THF (without using $\mathrm{Et_3N}$), it polymerized PyB into a polymer with a high M_{w} value (33300) in a high yield (80.5%; Table 1, no. 5). Solvent was again found to affect the alkyne polymerizations catalyzed by the zwitterionic complex, with the reaction rate changed in the following order: THF (fast) > DCM > toluene > 1,4-dioxane (slow).

Similar results were obtained for the polymerization of FcB monomer. On the basis of the polymerization results discussed above, it can be concluded that $\mathrm{Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]}$/THF is the best condition to be used for the polymerizations of the alkyne monomers.

Structural Characterization. Spectroscopic methods including IR and NMR were used to analyze the polymer structures. All the polymers as well as their monomers gave satisfactory characterization data corresponding to their expected molecular structures (see Experimental Section for details). An example of the IR spectrum of PPyB is shown in Figure 1; the spectrum of its monomer is also given in the same figure for the purpose of comparison. The monomer shows absorption bands at 3289 and 2116 $\mathrm{cm^{-1}}$, which are assignable to the stretching vibrations of ≡CH and C≡C, respectively. These bands are absent in the spectrum of PPyB, indicating that the triple bond of PyB has been consumed by the Rh-catalyzed alkyne polymerization reaction.

Figure 2 shows the ^{1}H NMR spectra of monomer PyB and its polymer PPyB. The spectrum of the monomer displays a strong single peak at δ 1.9, due to the resonance of its acetylene proton. This peak disappears in the spectrum of its polymer. A new peak associated with the resonance of olefinic proton is observed at δ 5.9.[30] This indicates that the acetylenic triple bond of the alkyne monomer has been transformed to the olefinic double bond in the polymer, consistent with the conclusion drawn from the IR spectral data discussed above.

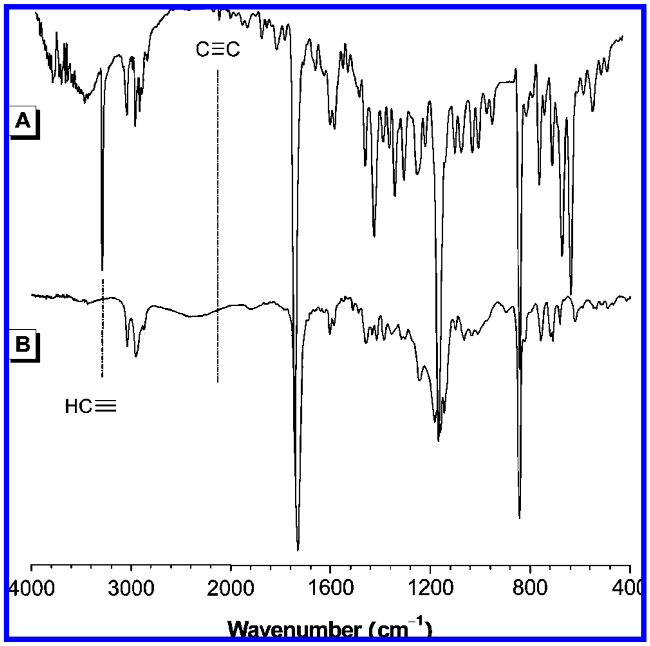


Figure 1. IR spectra of (A) monomer PyB and (B) its polymer PPyB.

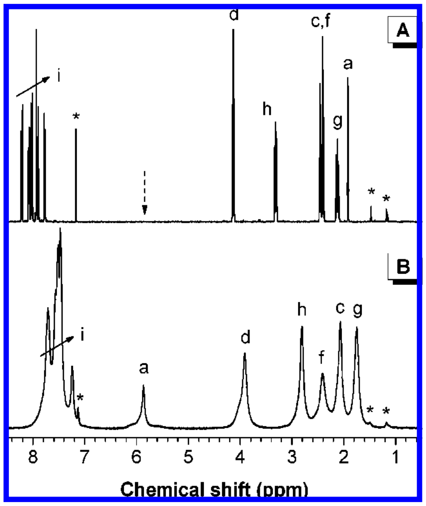


Figure 2. ^{1}H NMR spectra of (A) monomer PyB and (B) polymer PPyB in chloroform-*d*. The labels of the peaks correspond to those in Scheme 1. The peaks of solvent, water, and hexanes are marked with asterisks.

Figure 3 shows the ^{13}C NMR spectra of PyB and PPyB. Whereas the acetylenic carbon atoms of the monomer resonate at δ 69.9 and 80.1, these peaks are completely absent in the spectrum of the polymer. This once again confirms that the acetylene triple bond of the monomer has been consumed by the Rh-catalyzed alkyne polymerization. The polymerization changes the propargyl carbon to allylic carbon, hence the corresponding downfield shift of the resonance peak from δ 19.0 to 36.9.[31] All other peaks remain almost unchanged, especially the carbonyl resonance peak e, indicating that the Rh-catalyzed alkyne polymerization is triple bond-selective and is harmless to other functional groups.

Polymer/CNT Hybridization. In our previous work, we found that the PPA chains could wrap around the CNT shells.[9a] What will happen if PPyB or PFcB is admixed with SWNT or MWNT? As can be seen from photographs A−D of Figure 4, the filtrated polymer/CNT mixtures are homogeneous and dark-

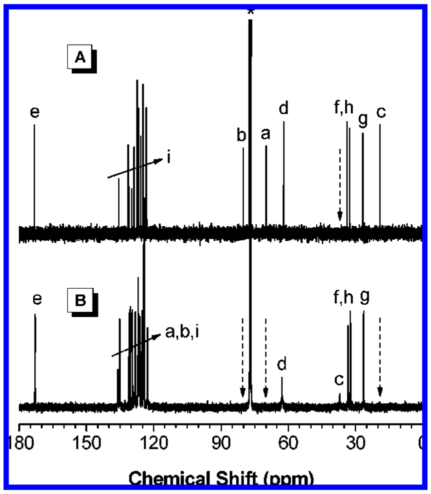


Figure 3. ^{13}C NMR spectra of (A) monomer PyB and (B) its polymer PPyB in chloroform-*d*. The labels of the peaks correspond to those in Scheme 1. The solvent peaks are marked with asterisks.

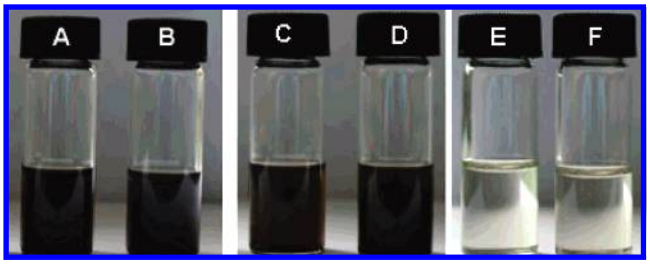


Figure 4. Photographs of THF solutions of (A) PPyB/SWNT, (B) PPyB/MWNT, (C) PFcB/SWNT, (D) PFcB/MWNT, (E) PClH(/SWNT), and (F) PClH(/MWNT). The undissolved CNTs were removed by filtration.

colored. Because the THF solutions of the pure polymers are colorless or light yellow, the dark colors of the solutions manifest that the CNTs have been brought into the liquid media by the solvation through their interactions with the polymer chains.

Following the same mixing and filtration procedures, homogeneous solutions of PPyB/CNT hybrids in other common organic solvents such as chloroform, DCM, DMF and DMSO were obtained. The hybrid solutions were stable and could stand for weeks without precipitation. The dried hybrid powders could be redispersed in common organic solvents. The PFcB/CNT hybrids showed similar dissolution behaviors. The good solubility, long-term stability, and solvent redispersibility bestow the hybrids with fine processability, paving the way toward potential technological applications.

TEM was used to examine the morphology of the polymer/CNT hybrids. As shown in Figure 5, both SWNT and MWNT are thickly wrapped or coated by the polymer chains. The polymer layers in the PPyB/SWNT, PPyB/MWNT, PFcB/SWNT, and PFcB/MWNT composites are about 40, 90, 50, and 75 nm in thickness, respectively. The thick wrapping or coating indicates good adherence of the polymers to the CNTs and strong interactions between the polymer chains. In comparison to those on the SWNTs, the polymer layers on the MWNTs are generally thicker and more uniform, probably because the bigger diameters, and hence smaller curvatures and more surface areas, of the MWNTs have allowed more polymer chains to wrap around or coat on their shells.

Solvating Power. As discussed above, the pyrene- and ferrocene-containing poly(1-alkyne)s can be used as dispersants to assist the dissolution of CNTs in common organic solvents.

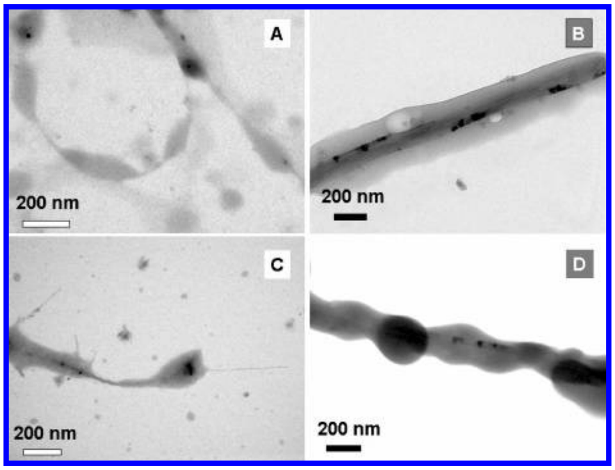


Figure 5. TEM images of nanohybrids of (A) PPyB/SWNT, (B) PPyB/MWNT, (C) PFcB/SWNT, and (D) PFcB/MWNT. The samples were taken from their dilute THF solutions.

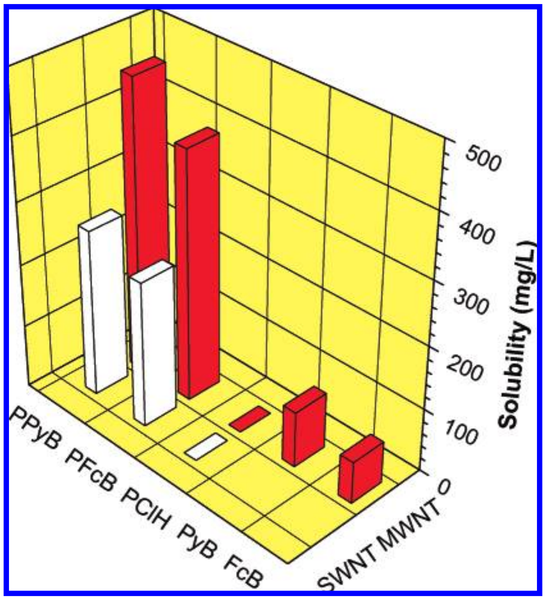


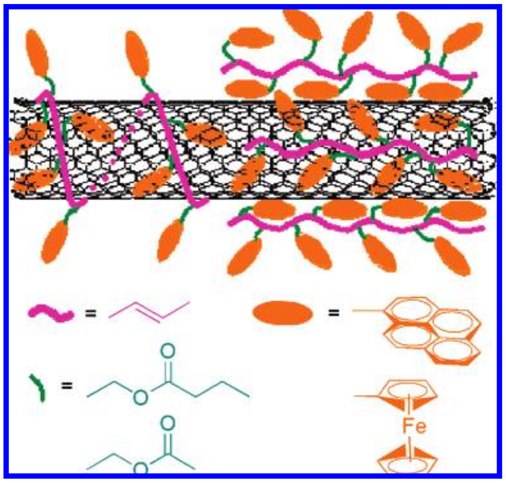
Figure 6. Comparison of the solubilities of SWNT and MWNT in THF in the presence of monomers FcB and PyB and polymers PClH, PFcB and PPyB.

To quantitatively evaluate the solvating powers of the polymers, we measured the solubilities of the hybrids in THF by using eq 1. We also conducted the solubility tests on the monomers (PyB and FcB) and a poly(1-alkyne) carrying no aromatic pendant (PClH). All the measurements were done under identical conditions to make sure that the obtained solubility data can be compared with each other.

From the data plotted in Figure 6 and the photos shown in Figure S2 (Supporting Information), one can see that both of the two monomers can help disperse MWNT in THF. The solvating powers of the monomers are, however, rather low, in comparison to those of their polymers. The solubilities of the FcB- and PyB-functionalized MWNTs are 67 and 89 mg/L, while those of the PFcB- and PPyB-functionalized MWNTs are 400 and 467 mg/L, respectively. Theses larger than 5-fold increases in the solubilities indicate that there is a profound “polymer effect” in the CNT solvation process.

The data in Figure 6 also reveal that the solvating power of the polymer is greatly dependent on its pendant. The poly(1-alkyne) bearing no aromatic pendant (PClH) cannot help disperse CNTs in THF at all (cf., photos E and F in Figure 4).

Chart 1



On the other hand, the polymers carrying aromatic pendants of Py and Fc rings can assist the dissolution of large amounts of CNTs into the organic solvent. Clearly, it is the aromatic pendants that have made the polymers good dispersants. Similarly to the monomers, the polymer carrying Py pendants exhibits higher solvating power than its counterpart carrying Fc pendants.

Mechanism of CNT Solubilization. The solubilization of CNTs may be realized through following mechanism: the polymer chains are attracted to the CNT shells due to the strong electronic interactions between the aromatic pendants and the CNT surfaces (Chart 1), and the affinity of the polymer chains with the solvent molecules brings the polymer-wrapped or -coated CNTs into the liquid media, leading to the dissolution of CNTs in the organic solvents.

The pyrenyl pendant is a bigger aromatic system than the ferrocenyl one, which explains why PPyB is a better dispersant than PFcB. When the polymer chains carrying the aromatic pendants stick to or wrap around CNTs, it brings many aromatic rings into close contact with the CNT shells. The polymer chains stuck to the CNT surfaces can attract other polymer chains via pendant−pendant electronic interactions, resulting in a thick coating of many polymer chains round the CNT shells. This is probably the cause of the observed “polymer effect”. The backbone of PClH possesses a short effective conjugation length and its electronically inactive alkyl pendants impede its polyene backbone from accessing to the CNT shells. This accounts for its inability of solvating the CNTs.

Raman Spectral Study. To study the electronic interactions between the polymers and the CNTs, Raman spectra were recorded. It is known that perturbations to the electronic structures of CNTs can be traced by the changes in the positions and intensities of their Raman bands.[10a,32] The pristine SWNT shows two G bands at 1550 and 1575 cm^{-1} (Figure 7A), which correspond to the splitting of the optical phonon or the E_{2g} mode in the graphite structure into longitudinal components at higher energies and transverse ones at lower energies.[9c] In addition, a weak, broad D band is observed at 1402 cm^{-1}. PPyB shows three bands at 1237, 1401, and 1622 cm^{-1} due to the vibrations of its C═C bonds.

In the spectrum of PPyB/SWNT hybrid, four bands are observed at 1237, 1390, 1594, and 1624 cm^{-1} (Figure 7C). The peaks at 1624 and 1594 cm^{-1} are assignable to the C═C stretching of PPyB and the G band of SWNT, respectively. It seems that the two G bands of SWNT have merged into a new one that locates at a higher frequency. The intensities of the bands at 1237 and 1390 cm^{-1} are much higher than those of PPyB. Perturbations to CNT structures are often accompanied by increases in the intensities of the D bands at 1250−1450 cm^{-1}.[33] The intensity increase in the D bands observed in the PPyB/SWNT hybrid here may thus be due to the release of individual SWNT from the agglomerative bundles and hence the dislocation of more surface defects. The Raman spectral data indicate that the CNTs are well dispersed in the hybrid, consistent with the TEM observations (cf., Figure 5). It is also noticeable that the D band has shifted by as large as 12 cm^{-1}. The frequency shift and the intensity increase in the D band manifest the strong electronic interactions between the polymer and the SWNT.

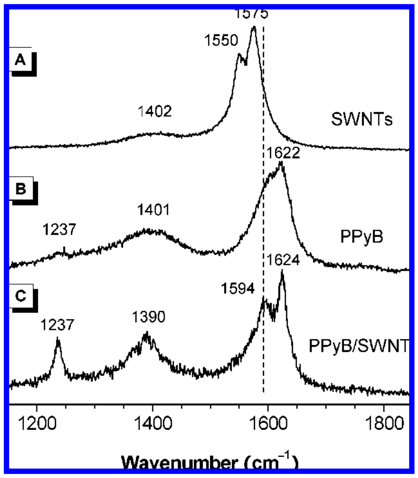


Figure 7. Raman spectra of (A) SWNT, (B) PPyB, and (C) PPyB/SWNT.

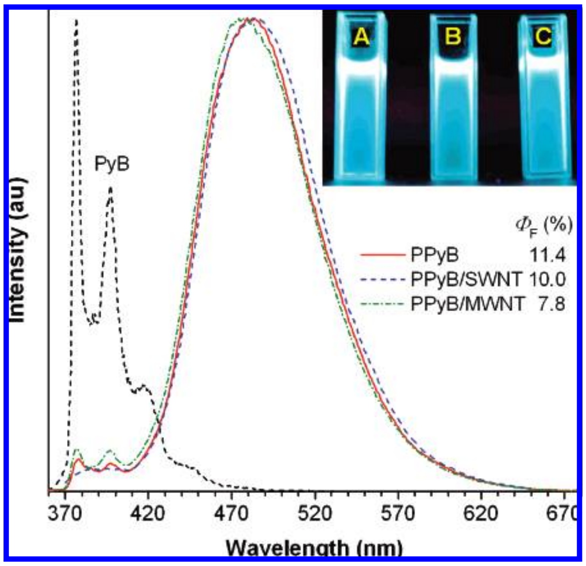


Figure 8. Emission spectra of PyB, PPyB, PPyB/SWNT, and PPyB/MWNT in THF. Concentration: 1 μg/mL. Excitation wavelength: 345 nm. Inset: Photographs of the THF solutions of (A) PPyB, (B) PPyB/SWNT and (C) PPyB/MWNT taken under a UV illumination.

Light Emission. The strong electronic interactions bestowed CNTs with not only desired solubility but also added functionality. Pyrene is a famous luminophore, whose dilute and concentrated solutions exhibit “monomer” and “excimer” emissions in the UV and visible regions, respectively.[9b,34] Upon photoexcitation, the dilute solution of PyB shows two monomer emissions at 377 and 397 nm, with no excimer emission observed (Figure 8). The spectrum of the PPyB solution is, however, dominated by the excimer emission at 484 nm, with

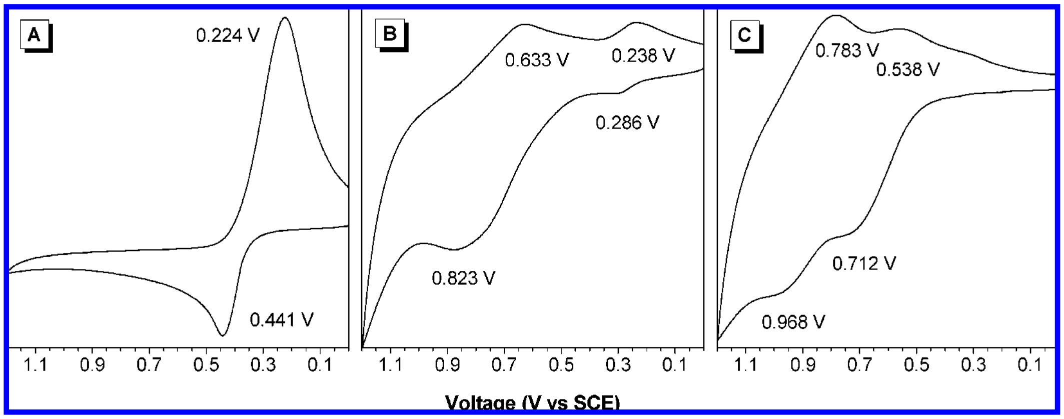
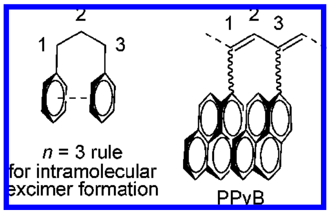


Figure 9. Cyclic voltammograms of (A) PFcB, (B) PFcB/SWNT, and (C) PFcB/MWNT taken in DCM containing 0.2 M Bu_4NClO_4 at a scan rate of 50 mV/s. The CV curves were recorded after removing the unbound, free polymers by repeated washing of the hybrids through 0.22 μm filters.

Chart 2



the monomer emissions became hardly discernible, although the concentration of the PPyB solution is as low as that of the PyB solution (2.94 μM). This indicates that the pyrenyl pendants in the immediate neighborhood along the polymer chain have experienced strong intramolecular interaction and formed intramolecular excimer species (Chart 2), following the well-known $n = 3$ rule discussed in our previous paper.[19e]

CNTs are nonemissive but their hybrids with PPyB are luminescent. The photoluminescence spectra of PPyB/CNTs are similar to that of PPyB, also dominated by the pyrene excimer emission (Figure 8). The fluorescence quantum yields (Φ_F) of PPyB/SWNT and PPyB/MWNT are somewhat lower than that of PPyB, indicative of an emission quenching, which has been commonly observed in CNT hybrids.[13b] The emission quenching is caused by the electron or energy transfer between PPyB and CNTs, further confirming the existence of the pendant−CNT interactions.

Redox Activity. We have just shown that CNTs can be made fluorescent by their hybridizations with PPyB because the pyrenyl pendants of the polymer coats are emissive. It is reasonable to conceive that the PFcB/CNT hybrids are redox active, because ferrocene is a well-known redox-active group.[35] We examined the electrochemical behaviors of PFcB and its hybrids with CNTs in DCM. The results are shown in Figure 9. The PFcB solution exhibits one set of single redox waves and their related $E_{1/2}$ and $\triangle E_p$ values are 333 and 217 mV, respectively. The single peak indicates that there is no electronic communication between the neighboring iron centers.[36,37]

The PFcB/CNT hybrids, however, show quite different redox behaviors. The cyclic voltammograms of the PFcB/CNTs exhibit two sets of reversible redox waves (Figure 9, panels B and C), suggestive of existence of two different redox species in the hybrids.[36,38] As illustrated in Chart 1, some of the ferrocenyl pendants of PFcB are in close contact with the CNT shells, while some others are on the far side of the polyene backbone. These two groups of ferrocenyl pendants should experience different interactions with the CNTs, hence the observed two sets of redox waves.

Conclusions

In this work, we have synthesized two 1-butyne derivatives containing pyrene and ferrocene groups and investigated their polymerization behaviors. Among the organorhodium complexes studied, the zwitterionic species $Rh^+(nbd)[C_6H_5B^-(C_6H_5)_3]$ exhibited the highest efficiency in catalyzing the alkyne polymerizations in THF, furnishing corresponding pyrene- and ferrocene-containing poly(1-alkyne)s with high molecular weights in high yields.

Simple mixing of the polymers with the CNTs made the latter soluble in common organic solvents. The electronic interactions between the pendant groups of the polymers and the shells of CNTs were found to be responsible for the solvating process. A pronounced "polymer effect" was observed: the polymers were much better dispersants than their monomers, due to the cooperative interactions of the aromatic pendants in different polymer chains with the CNTs.

The polymers not only solubilized but also functionalized the CNTs. The pyrenyl and ferrocenyl pendants made the CNTs light-emitting and redox-active, respectively. This "pendant effect" prompts us to design and synthesize new substituted polyacetylenes containing other functional pendants, in an effort to prepare polymer/CNT hybrids with macroscopic processability and advanced functionalities.

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Supporting Information Available: Text describing the synthesis of PClH, a chart showing the chemical structures of the organorhodium catalysts used in this study, and figures showing TGA thermograms of PPyB and PFcB, photographs of the THF solutions of PPyB/MWNT, PFcB/MWNT, PyB/MWNT and FcB/MWNT hybrids, ^1H NMR spectra of PFcB and PFcB/MWNTs, and UV−vis absorption spectra of the monomers, polymers and hybrids. This material is available free of charge via the Internet at http://pubs.acs.org.

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