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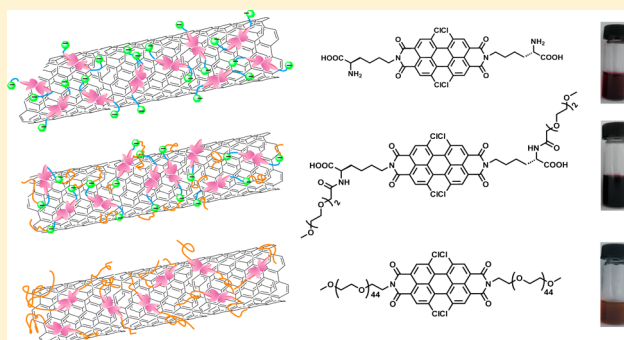
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S Supporting Information

ABSTRACT: The enhanced dispersing capability of these bolaamphiphiles can be attributed to the large aromatic perylene core. The aqueous dispersion efficiency of single-walled carbon nanotubes (SWCNTs) is investigated by UV–vis absorption, fluorescence emission and Raman spectra, scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. It is found that the tetrachloroperylene backbone moieties could interact with SWCNT via synergistic π – π and hydrophobic interactions, and the dispersing properties are closely related to the hydrophilic part of bolaamphiphiles. This study not only demonstrates tetrachloroperylene derivatives are able to stabilize SWCNTs, but also provides the possibility to understand the structure–property relationship between SWCNTs and tetrachloroperylene-based surfactants.



1. INTRODUCTION

Since first reported as “helical microtubules of graphitic carbon” by Iijima in 1991,¹ carbon nanotubes (CNT)^{1–3} have received extensive attention and opened a broad field of potential applications in nanoscience and nanotechnology, due to their extraordinary electronic,⁴ mechanical,^{5,6} and optical properties.⁷ However, their applications are limited by their poor solubility in solvents. Thus, improving CNTs’ solubility in solvent is of particular importance to expand their practical applications and processing.^{7–10} Notably, covalent modification^{11,12} and noncovalent absorption^{13,14} are two general routes for achieving CNT dispersion. Both strategies have their own advantages and disadvantages. Specifically, noncovalent absorption, which generally does not disrupt CNT’s electronic structure as well as physical properties, turns out to be an efficient method and economic strategy. Many dispersing systems have been investigated for the noncovalent modification of CNTs,^{15–17} such as surfactants,^{18,19} polymers,^{20,21} peptides,¹³ polycyclic aromatic hydrocarbons,^{17,22–25} and DNAs.^{26,27} Generally, these explored systems had amphiphilic characteristics. The protective core molecules anchor to the CNT’s surface via hydrophobic or/and π – π interactions, while the hydrophilic moieties confer them water solubility. Because the primary interactions for traditional surfactants are hydrophobic interactions, amphiphilic molecules containing macroaromatic core recently received active research interest because they can offer more specific π – π interactions with the π -electrons in CNT in addition to simple nonspecific hydrophobic

interactions. For instance, pyrene, porphyrin, and phthalocyanine derivatives were demonstrated to be efficient dispersants for SWCNTs for such reasons.^{17,24,25} In addition, perylene bisimide (PBI) and its derivatives were considered as efficient dispersants to stabilize SWCNT,²⁸ especially the amphiphilic PBI ones.^{3,29} For example, Hirsh and coworkers systematically studied a series of amphiphilic PBI derivatives modified by hydrophilic dendritic polyacids segments to disperse SWCNT in aqueous media and investigated the dispersing ability dependency on the molecular structure and the side chain.³ Recently, Ernst and coworkers utilized an amphiphilic perylene-based surfactant to disperse the carbon nanotubes and to form energy transfer complexes.³⁰

Furthermore, adding stimuli-responsive functionalities, such as pH or temperature, to the dispersion/assembly of SWCNTs would be desirable for advanced applications.³¹ For instance, poly-L-lysine-modified SWCNT displayed pH-sensitive dispersing capabilities,³² while poly(*N*-isopropylacrylamide)-modified SWCNT displayed temperature-sensitive dispersing characteristics.³² Therefore, design and synthesis of new amphiphilic molecules, which can efficiently disperse SWCNTs, are still greatly desirable.²⁰ Moreover, the systematic comparisons with different charge state have been rarely investigated. Herein, we synthesized three bolaamphiphilic surfactants containing PBI as

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73 core and three kinds of side chains, that is, zwitterionic, anionic,
74 and nonionic polymeric side chains. We investigated their
75 interactions with SWCNTs to control and manipulate the
76 dispersion and assembly behaviors of PBI functionalized
77 SWCNTs. The obtained dispersion could be stable for more
78 than 6 months.

2. EXPERIMENTAL SECTION

79 **2.1. Materials and Methods.** SWCNTs were purchased from
80 Acros (1–2 nm in diameter with lengths of 5–30 μm) and used as
81 received. 1,6,7,12-Tetrachloroperylene 3,4,9,10-tetracarboxylic acid
82 dianhydride (4CIPTCAD) was provided from Beijing Wenhaiyang
83 Industry&Trading Co., Ltd. \square Boc-L-lysine-OH was purchased from
84 GL Biochem (Shanghai) Ltd. Poly(ethylene glycol) methyl ether
85 amine (PEG-NH₂) ($M_n \approx 2000$) was purchased from Aladdin
86 Industrial Inc. Other reagents were purchased from Sinopharm
87 Chemical Reagent Co, Ltd. and used without further purification,
88 unless otherwise specified.

89 ¹H NMR spectra were recorded on a Bruker Avance DMX 400
90 MHz instrument using TMS as internal standard and D₂O as solvent.
91 MALDI-TOF-MS measurements were carried out using a Bruker
92 BIFLEX III equipped with a 337 nm nitrogen laser. UV–vis
93 absorption spectra (UV–vis) were recorded on a TU-1901
94 spectrophotometer. Fluorescence spectra were recorded on a Hitachi
95 F-4500 fluorescence spectrometer and corrected against photo-
96 multiplier and lamp intensity. The slit width of both monochromators
97 was 5.0 nm. Raman spectra were measured in solution by a RFS100/S
98 Raman spectrometer ($\lambda_{\text{exc}} = 1064 \text{ nm}$). Atomic force microscopy
99 (AFM) was performed in tapping mode (Multimode 8, Bruker, Inc.)
100 with silicon cantilever probes. The samples were prepared by casting
101 the sample solution on fresh peeled mica, and the scanning rate was 1
102 Hz. Transmission electron microscopy (TEM) samples were examined
103 with a JEM2200FS (200 keV). The surface microstructure was
104 examined via a scanning electron microscope (SEM) (6700F)
105 instrument.

106 **2.2. Synthesis of Three Bolaamphiphiles.** 4CIPBI-A. The
107 synthesis and structure characterization of 4CIPBI-A was reported
108 elsewhere.^{33,34}

109 **4CIPBI-B.** N-Hydroxysuccinimidyl PEG (PEG-NHS) was synthe-
110 sized according to the literature.³⁵ 4CIPBI-A (5.00 g, 6.4 mmol) and
111 PEG-NHS (4.37 g, 15.9 mmol) were mixed with Et₃N (1.6 g, 15.9
112 mmol) in methanol (150 mL). The reaction mixture then was stirred
113 at room temperature for 24 h. After being filtered, the solution was
114 concentrated and treated with pH = 1 HCl solution. The product was
115 obtained as a red solid, which was subsequently washed with water
116 three times. The 4CIPBI-B then was purified by column chromatog-
117 raphy on silica gel to give an orange powder (4.4 g, yield 62%,
118 methanol/CH₂Cl₂ = 1/10). ¹H NMR (400 MHz, D₂O, δ): 8.6 (s,
119 4H), 7.4 (m, 2H), 4.5 (m, 2H), 3.9–3.3 (m, 22H), 3.2 (m, 6H), 1.8–
120 1.2 (m, 12H). ¹³C NMR (400 MHz, acetone-*d*₆, TMS): 189, 162, 134,
121 128, 126, 123, 109, 92, 90, 82, 74, 70, 60, 58, 51, 46, 30, 29, 28 ppm.
122 MALDI-TOF (m/z): calcd for C₅₀H₅₂Cl₄N₄O₁₆, 1104.2; found,
123 1104.7.

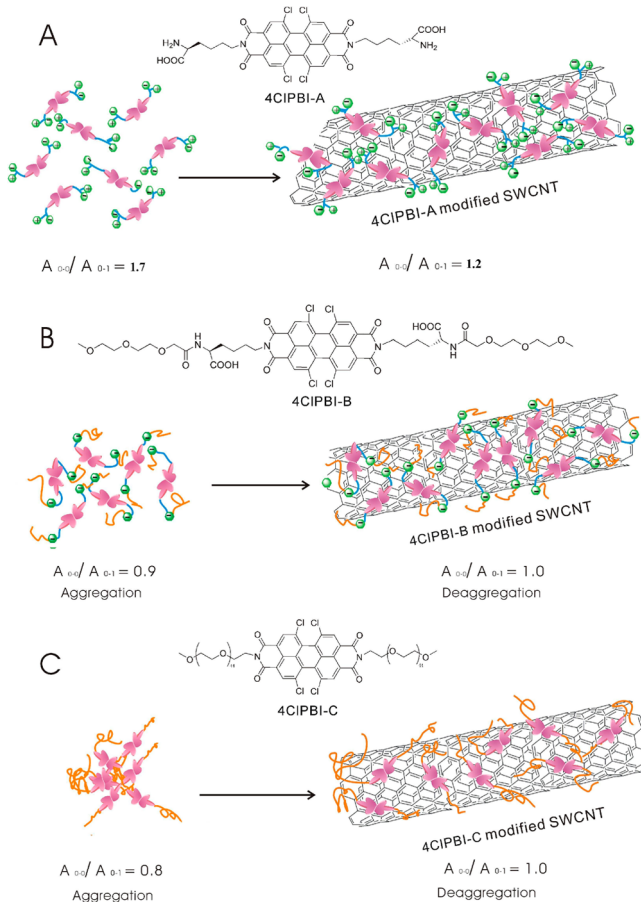
124 **4CIPBI-C.** PEG-NH₂ (2.00 g, 1.0 mmol) and 4CIPTCAD (176 mg,
125 0.33 mmol) were mixed in ethanol (50 mL), and then the reaction
126 mixture was refluxed for 24 h. Orange precipitate was filtrated, dried in
127 vacuum, and then was further purified by column chromatography on
128 silica gel to give an orange powder (1.01 g, yield 76%, methanol/
129 CH₂Cl₂ = 1/5). ¹H NMR (400 MHz, CDCl₃, δ): 8.68 (s, 4H), 4.46
130 (m, 4H), 3.84 (m, 6H), 3.64–3.37 (br, 323H), 1.25 (s, 6H). ¹³C NMR
131 (400 MHz, CDCl₃, δ): 173, 166, 162, 158, 152, 138, 135, 132, 131,
132 128, 127, 123, 113, 74, 67, 57.

133 **2.3. General Procedure for Dispersing SWCNTs.** Typically,
134 SWCNTs and 4CIPBI-A/B/C were mixed into 4 mL of pH = 10
135 buffered aqueous solution with a weight ratio of 1:1, stirred for 10 min
136 and sonicated for 1 h, followed by centrifugation (5000 rpm, 5 min).
137 The samples with different SWCNT concentration were also
138 conducted by this method.

3. RESULTS AND DISCUSSION

Following the reported procedure,³⁴ we synthesized three
139 bolaamphiphiles using tetrachloroperylene bisimide as core.
140 These three bolaamphiphiles with chemical structure illustrated
141 in Scheme 1 were designated as 4CIPBI-A (zwitterionic),
142 s1

Scheme 1. Mechanism for the Interaction between SWCNT and (A) 4CIPBI-A, (B) 4CIPBI-B, and (C) 4CIPBI-C



4CIPBI-B (anionic), and 4CIPBI-C (nonionic polymeric). The
143 synthesized bolaamphiphiles contained a polycyclic aromatic
144 core aiming for π – π interaction with SWCNT, while the
145 terminal hydrophilic segments albeit with distinct chemical
146 nature were designed to confer water solubility and protect
147 dispersed SWCNTs from agglomeration. For 4CIPBI-A, the ϵ -
148 amine group of L-lysine was conjugated to the imide position of
149 4CIPBI to obtain a symmetric bolaamphiphile with 4CIPBI as
150 hydrophobic core and lysine as hydrophilic heads. Our previous
151 study showed that 4CIPBI-A can self-assemble into 2-D
152 monolayer film at pH ranging from 1 to 9.³⁴ For 4CIPBI-B,
153 we introduced an oligo(ethylene glycol) (OEG) to the end
154 amine group of 4CIPBI-A, which made 4CIPBI-B into an
155 anionic bolaamphiphiles. For 4CIPBI-C, we replaced the lysine
156 moiety in 4CIPBI-A with poly(ethylene glycol) (PEG), and
157 obtained a polymeric bolaamphiphile. We then used the above
158 three bolaamphiphiles as dispersants to stabilize SWCNTs, and
159 investigated the correlation between surfactants' end-groups
160 and dispersing efficiency. For the dispersing experiments,
161 SWCNTs were simply mixed with three bolaamphiphiles under
162 sonication, and then the mixtures were characterized using
163 spectroscopy and electron microscopy.
164

We first investigated the solution of 4CIPBI-A and SWCNT at the weight ratio of 1:1. Because the aggregation behaviors of 4CIPBI-A depended on solution pH value, we conducted the experiment at pH = 10 to avoid undesired self-aggregation of 4CIPBI-A.³⁴ The SWCNTs were added into the 4CIPBI-A aqueous solution under sonication and followed by centrifugation. The supernatant was then separated and characterized. The successful dispersion of SWCNTs by 4CIPBI-A was first demonstrated by visual observation (Supporting Information Figure S1a). Pristine SWCNT was phase separated from water without dispersant, while the water solution of 4CIPBI-A at pH = 10 was pink. In contrast, their mixture displayed dark purple color, indicating the absorption of 4CIPBI-A onto SWCNT, and their interactions were further verified by spectroscopy characterizations. It was known that the ratio of absorbances at 544 nm (A_{0-0}) and 502 nm (A_{0-1}) reflected the physical status of the 4CIPBI molecule.³⁶ Before SWCNTs were added, the A_{0-0}/A_{0-1} ratio for 4CIPBI-A solution was 1.8 (Figure 1a), but

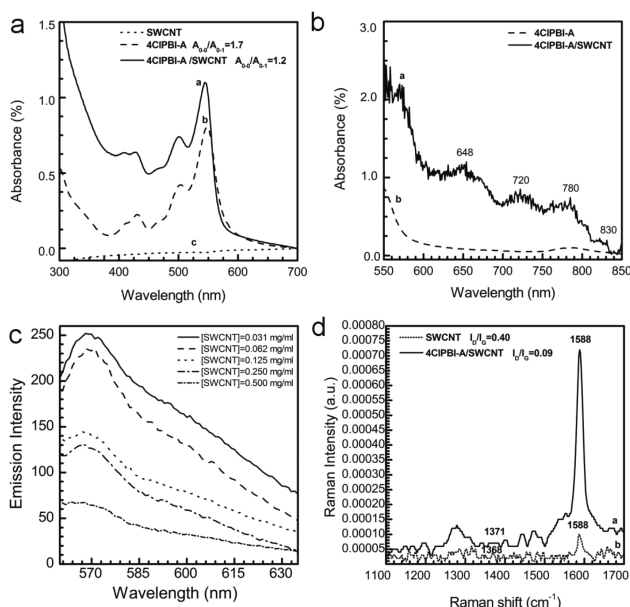


Figure 1. Absorption spectra of SWCNT, 4CIPBI-A, and the mixture of 4CIPBI-A/SWCNT = 1/1: (a) 0.1 mg/mL and (b) 0.19 mg/mL; (c) the fluorescence emission spectra of 4CIPBI-A/SWCNT with different SWCNT concentrations at $\lambda_{\text{ex}} = 545$ nm; and (d) the Raman spectra of SWCNT and 4CIPBI-A/SWCNT = 1/1 (0.1 mg/mL). All of the samples were prepared in pH = 10 aqueous solution.

it decreased to 1.3 after mixing 4CIPBI-A with SWCNTs, which could be attributed to the strong π - π interactions between 4CIPBI core and SWCNTs. Meanwhile, as shown in Figure 1b, the absorption spectrum of SWCNTs with/without 4CIPBI-A can also reflect its dispersing status. Individual 4CIPBI-A did not show any characteristic absorption in the range of 550–900 nm. The mixture of 4CIPBI-A and SWCNT displayed four peaks in this region, that is, 648, 720, 780, and 830 nm, which were related to the SWCNT's von Hove singularities and indicated the homogeneous dispersion of SWCNTs in aqueous solution.^{13,22,37–40}

The fluorescent spectrometer was applied to characterize the interactions between 4CIPBI core and SWCNT. As shown in Figure 1c, we kept the concentration of 4CIPBI-A at 0.125 mg/mL, and found its fluorescence intensity decreased gradually with the increase of SWCNT concentration, which was

attributed to the expansion of delocalized π -electron system among perylene cores and SWCNTs. It also supported that free 4CIPBI-A molecules were adsorbed onto SWCNTs.⁴¹ The effects of SWCNTs' concentrations on the absorption spectra were compared in Supporting Information Figure S2a. With the increase of SWCNT's concentration from 0.031 to 0.062 and to 0.125 mg/mL, the value of A_{0-0}/A_{0-1} decreased from 1.8 to 1.7 and to 1.4, respectively, which indicated that the interactions among perylene cores became weaker and weaker. Notably, when the SWCNTs concentration was higher than 0.125 mg/mL, the A_{0-0}/A_{0-1} value maintained as 1.4, which may be attributed to the adsorption equilibrium of 4CIPBI-A onto SWCNTs.

It is well-known that Raman spectroscopy is a suitable technique to characterize dispersed SWCNTs and their aggregates.⁴ Generally, the intensity of the G-band (I_G) reflects the content of individual SWCNT, while the D-band value (I_D) corresponds to the impurities, for example, aggregates. For the mixture of 4CIPBI-A/SWCNT, the I_D/I_G ratio decreased from 0.4 to 0.08 with the addition of 4CIPBI-A (Figure 1d). The obvious decrease of the I_D/I_G ratio and the increased intensity of RBM region in Raman spectra (Supporting Information Figure S1c) demonstrated that the SWCNT bundles were effectively exfoliated by 4CIPBI-A bolaamphiles.⁴²

Finally, the effective dispersion of SWCNTs by 4CIPBI-A was directly visualized using electron microscopy technique. Figure 2 compared the TEM images of SWCNT before and

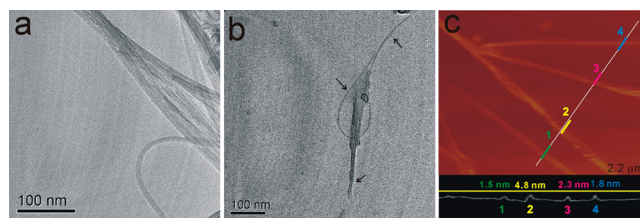


Figure 2. TEM image of SWCNT before (a) and after (b) the addition of 4CIPBI-A; and (c) AFM image and height profile of 4CIPBI-A/SWCNT = 1/1 (1 mg/mL).

after mixing of 4CIPBI-A. Before adding 4CIPBI-A, SWCNTs existed as aggregated bundles. Upon mixing with 4CIPBI-A aqueous solution, SWCNTs were observed as isolated tubes with length of approximately 500 nm. Similar results were further supported from AFM characterization (Figure 2c), which revealed the elongated SWCNTs with height ranging between 1.5 and 4.8 nm, suggesting the successful dispersion by 4CIPBI-A.

Besides zwitterionic 4CIPBI-A, the anionic 4CIPBI-B and nonionic 4CIPBI-C can also effectively disperse SWCNTs in water. Given the procedure identical to that of 4CIPBI-A, the SWCNTs were added into the 4CIPBI-B aqueous solution at pH = 10. After that, the mixture's solution color changed from scarlet to dark purple (Supporting Information Figure S3a). The variations of physical status about 4CIPBI-B and SWCNTs were further demonstrated by spectroscopy characterizations. In Figure 3a, the A_{0-0}/A_{0-1} ratio of pristine 4CIPBI-B was 0.9, and this value increased to 1.0 after 4CIPBI-B was adsorbed on the nanotube sidewall.^{3,28,43} These results revealed that SWCNTs also could be well-dispersed by anionic 4CIPBI-Bs. The further spectroscopic observations proved that the SWCNT bundles were exfoliated well after the addition of 4CIPBI-B, including the characteristic signal of van Hove transitions for

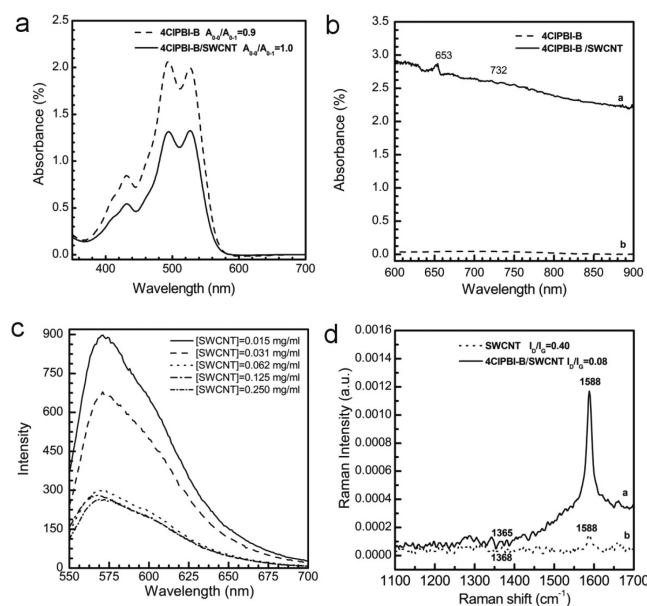


Figure 3. Absorption spectra of 4CIPBI-B and the mixture of 4CIPBI-B/SWCNT = 1/1: (a) 0.1 mg/mL and (b) 0.33 mg/mL; (c) the fluorescence emission spectra of 4CIPBI-B/SWCNT with different SWCNT concentrations at $\lambda_{\text{ex}} = 530$ nm; and (d) the Raman spectra of SWCNT and 4CIPBI-B/SWCNT = 1/1 (0.1 mg/mL). All of the samples were prepared in pH = 10 aqueous solution.

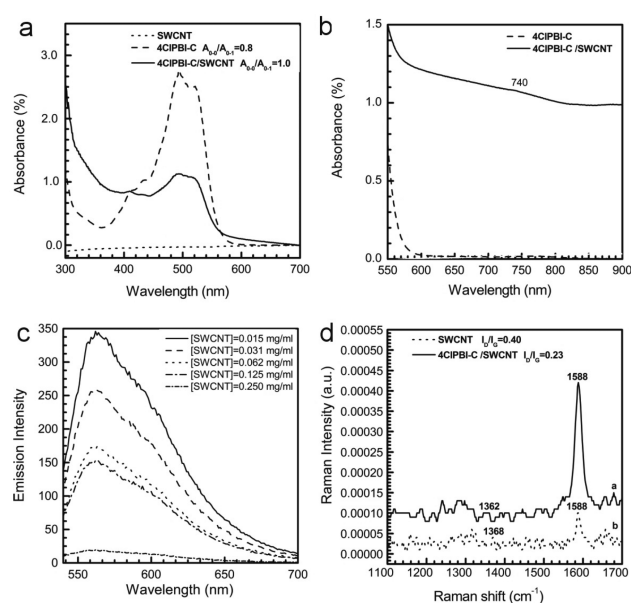


Figure 4. Absorption spectra of SWCNT, 4CIPBI-C, and the mixture of 4CIPBI-C/SWCNT = 1/1: (a) 0.1 mg/mL and (b) 0.33 mg/mL; (c) the fluorescence emission spectra of 4CIPBI-C/SWCNT with different SWCNT concentrations at $\lambda_{\text{ex}} = 520$ nm; and (d) the Raman spectra of SWCNT and 4CIPBI-C/SWCNT = 1/1 (0.1 mg/mL). All of the samples were prepared in pH = 10 aqueous solution.

SWCNTs^{13,22,37–40} in absorption spectra (Figure 3b), the dropping intensity of the free perylene in the emission spectra⁴¹ (Figure 3c), and the decreasing I_D/I_G ratio⁴² in Raman spectra (Figure 3d). Besides, the TEM and AFM results verified the dispersed nanotube in Supporting Information Figure S4.

For nonionic 4CIPBI-C, the photos of the SWCNT, 4CIPBI-C, and 4CIPBI-C/SWCNT shown in Supporting Information Figure S5a implied the uptake of SWCNT in aqueous solution. Given the amphiphilic feature, 4CIPBI-C was supposed to self-assemble into aggregates in water, and the A_{0-0}/A_{0-1} ratio was only 0.8 (Figure 4a). After the addition of SWCNTs, the A_{0-0}/A_{0-1} ratio increased to 1.0, which implied the disassembly of preformed aggregates upon the interaction with SWCNTs. The further spectroscopic studies also verified the successful dispersion, such as the typical SWCNT van Hove singularities from absorption spectra (Figure 4b), the decrease of free 4CIPBI-C with the addition of SWCNT in the emission spectra (Figure 4c), and the reducing I_D/I_G ratio and the RBM region of SWCNTs in Raman spectra (Figure 4d and Supporting Information Figure S5c, respectively). Furthermore, the electron microscopic results also demonstrated the exfoliated SWCNTs in 4CIPBI-C aqueous solution (Supporting Information Figure S6).

Note that the dispersion rates of SWCNTs in these three amphiphile aqueous solutions were different. Among them, 4CIPBI-A was the fastest, while 4CIPBI-C was the slowest. We presumed that the most important influence on the aqueous dispersibilities of PBI modified SWCNTs was due to the terminal structures of three amphiphiles, because they shared the same perylene core to provide $\pi-\pi$ interactions with SWCNTs. The mechanism of the 4CIPBI-A modified SWCNT was presented in Scheme 1. Initially, 4CIPBI-A in the solution was monomeric form due to the static repulsion caused by lysine; however, after the addition of SWCNT, the aromatic interaction between perylene cores and nanotube's sidewall

resulted in the adsorption. Meanwhile, charged lysine helped to stabilize the SWCNTs in aqueous solution. Therefore, the distances among 4CIPBI-A monomers were gradually shortened after the adsorption onto SWCNTs, and a bigger delocalized π -conjugated system formed between SWCNTs and PBI cores, which led to the decrease of the A_{0-0}/A_{0-1} ratio. Furthermore, the negative charged lysine side chains prevented these molecules from being close to each other, which was reflected by the ratio of A_{0-0}/A_{0-1} that was still above 1. For anionic 4CIPBI-B in aqueous solution (Scheme 1B), it could self-assemble into aggregates even at pH 10. With the addition of SWCNTs, the $\pi-\pi$ interactions between 4CIPBI-B and SWCNTs were stronger than that among pristine 4CIPBI-Bs or SWCNTs, which led to the disaggregation of preformed 4CIPBI-B assemblies and the dispersion of SWCNTs. For nonionic 4CIPBI-C (Scheme 1C), due to the distinct steric hindrance of the long PEG side chains, the $\pi-\pi$ interactions were dramatically weakened between 4CIPBI-Cs and SWCNTs. So, as compared to 4CIPBI-A and 4CIPBI-B, its dispersing effect was the worst.

4. CONCLUSION

In summary, we have succeeded in dispersing SWCNTs using three kinds of bolaamphiphiles, that is, zwitterionic 4CIPBI-A, anionic 4CIPBI-B, and nonionic polymeric 4CIPBI-C, in aqueous solution through sonication and centrifugation procedure. The combination of $\pi-\pi$ stacking, van der Waals forces, and hydrophobic interactions could generate the efficient dispersion of SWCNTs. However, they also generated different dispersing abilities due to their distinct end groups. Especially, zwitterionic 4CIPBI-A was the most efficient dispersant, followed by anionic 4CIPBI-B, and nonionic 4CIPBI-C was the worst. Besides, the different ambient conditions, such as pH and temperature, might assist the further assembly of dispersed SWCNTs, which paves a new way

for dispersing and manipulating SWCNTs and might have potentials in sensing, drug delivery, and nanodevices.

■ ASSOCIATED CONTENT

● Supporting Information

Additional spectroscopy and electron microscopy characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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