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Porphyrin−Carbon Nanotube Composites Formed by Noncovalent Polymer Wrapping

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Stable porphyrin/single-walled nanotube (SWNT) composites were synthesized by condensation of tetraformylporphyrins and diaminopyrenes on SWNTs. The degree of interaction between SWNTs and porphyrin was evaluated by UV−vis and fluorescence spectra, and chemical removal of porphyrin from SWNTs. In the composites, the Soret and Q-bands of porphyrin moieties were significantly broadened and their fluorescence was almost quenched. Apparent extinction coefficients at the Soret bands of the composites were decreased to ca. 20%.

Introduction

Carbon nanotubes (CNTs) discovered by Iijima[1] have excellent electronic properties.[2] In particular, semiconducting CNTs are useful in various applications, such as field effect transistors (FETs)[3] and photoresponsive devices.[4] Combination of organic dyes and semiconducting CNTs enables the use of photovoltaic devices for visible light applications.[5] Thus, various methods of CNT modification using covalent[6] and noncovalent approaches[7,8] have been reported. Noncovalent methods are preferable because they allow the excellent electronic properties of CNTs to be retained, while covalent modification effectively destroys the continuous π-system of CNTs. Noncovalent modifications involving dyes have used polymers such as poly-*m*-phenylenevinylene (PmPV)[9] and molecules with a large π-system, such as pyrene,[10] anthracene,[11] phthalocyanine,[12] and porphyrin.[13] Interestingly, in the PmPV/CNT composite system, conductivity was found to increase on light irradiation at the absorption band of PmPV.[9c,14] When we examine such a dye-sensitizing property in composites, it is important to know the electronic properties of the dye on CNT. Although absorption spectra of dye/CNT composites are shown in some cases,[9c,10d,11,12,13a] peaks corresponding to the dye are unclear or hardly detectable. The difficulty associated with their observation is attributed to the decrease in the extinction coefficient, variation of the spectral shape on the CNT surface, and/or the limited amount of dye in contact with CNT. Porphyrin is known as a good photosensitizer, and has a sharp Soret band with an extremely large extinction coefficient as well as other characteristic absorption bands in solution. Therefore, porphyrin on CNTs is expected to

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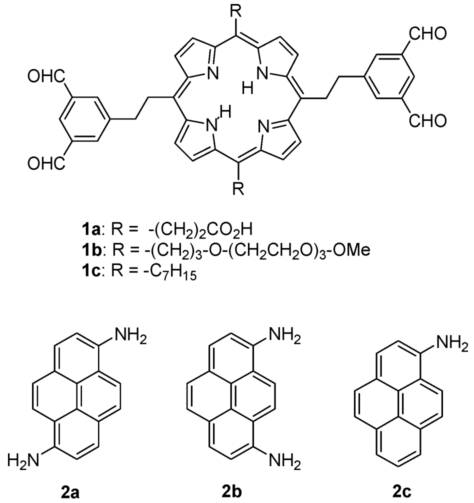
Scheme 1. Tetraformylporphyrins 1a−c and Diaminopyrenes 2a−c



perform well as a sensor for sensing the electronic state in the environment if composites with a sufficient amount of porphyrin can be isolated. In this paper, we report noncovalent polymer wrapping of CNTs by simple condensation products of tetraformylporphyrins **1a**, **1b**, and **1c** with diaminopyrenes **2a**, **2b**, and **2c** (Scheme 1). This method has proven effective in bringing porphyrin into strong, but noncovalent, interaction with CNTs. Since free, weakly bound porphyrin can be washed away, only porphyrin bound strongly with CNT is differentiated. The data reported in the present study clearly show that the absorption spectra of porphyrin/CNT composites are significantly different from those in solution.

Experimental Section

Preparation of Materials. *General Procedures.* ^{1}H NMR spectra were recorded on a JEOL EX-270 (270 MHz) or ECP-600 (600 MHz) spectrometer using TMS (0 ppm) or the residual proton resonance (7.26 ppm for $CHCl_3$, 8.71, 7.56, and 7.19 ppm for pyridine-d_5) of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). MALDI TOF mass spectra were obtained with a Perseptive Biosystems Voyager DE-STR with dithranol (Aldrich) as a matrix. UV−vis and near-IR spectra were obtained with a Shimadzu UV-3100PC spectrometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrometer. IR spectra were obtained with a Nicolet AVATAR 320ES FT-IR. Resonance Raman spectra were measured by a JASCO NRS-2100 with a COHERENT INNOVA 70C Ar ion laser (at 514.5 nm). Atomic force microscope (AFM) images were obtained on a Nanoscope IIIa (Digital Instruments Co.) according to tapping mode with a Si cantilever (spring constant of 16 N m^{-1}, tip curvature radius of 5−10 nm). Transmission electron microscope (TEM) images were obtained on a JEM-3100FEF (JEOL Co.) Column chromatography was performed with silica gel (63-210 μm, KANTO Chemical Co., Inc.). All chemicals obtained from commercial sources were used without further purification, unless otherwise mentioned. The single-walled carbon nanotube (SWCNT) was purchased from Rice University. 1-Aminopyrene, 1,6-diaminopyrene, and 1,8-diaminopyrene were synthesized according to the literature.[15]

Preparation of Porphyrins. Tetraformylporphyrins **1a**, **1b**, and **1c** were prepared as illustrated in Schemes 2, 3, and 4.

5-Hydroxyisophthalic Acid Diethyl Ester 3. A mixture of 5-hydroxyisophthalic acid (10.5 g, 57.5 mmol) and H_2SO_4 (3.3 mL) in EtOH (200 mL) was refluxed for 39 h. After evaporation of EtOH, the colorless solid was washed with water and dried under reduced pressure at 60 °C to give diester **3** (12.5 g, 93%). TLC $R_f = 0.5$ (hexane/AcOEt = 2/1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.26 (1H, s, phenyl H), 7.75 (2H, s, phenyl H), 4.41 (4H, q, $J = 7.0$ Hz, $-OCH_2CH_3$), 1.41 (6H, t, $J = 7.0$ Hz, $-OCH_2CH_3$). mp 98−100 °C.

3,5-Diethoxycarbonyl-1-trifluoromethanesulfonyloxybenzene 4. Diester **3** (8.4 g, 35.4 mmol) was dissolved in EtOH-free $CHCl_3$ (60 mL) prepared by passing through Al_2O_3. 2,4,6-Trimethylpyridine (18.7 mL, 142 mmol) was added, and the mixture was cooled at 0 °C. Trifluoromethanesulfonic anhydride (10 g, 35.4 mmol) was added, and the mixture was stirred at 0 °C. After 2 h, ice bath was removed, and the mixture was stirred for 20 h at room temperature. $CHCl_3$ was evaporated under reduced pressure, and water (50 mL) was added to the mixture. Organic layer was extracted with hexane/ethyl ether = 2:1, and the organic layer was washed with aqueous $CuSO_4$ solution and water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/ether = 9:1−6:1) to give triflate **4** (8.3 g, 64%). TLC $R_f = 0.7$ (hexane/AcOEt = 2:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.70 (1H, s, phenyl H), 8.10 (2H, s, phenyl H), 4.45 (4H, q, $J = 7.0$ Hz, $-OCH_2CH_3$), 1.43 (6H, t, $J = 7.0$ Hz, $-OCH_2CH_3$). mp 42−43 °C.

Methyl 3-(3,5-Diethoxycarbonylphenyl)-2-propenoate 5. Palladium acetate (84 mg, 0.38 mmol) and bis(diphenylphosphino)-propane (160 mg, 0.39 mmol) were mixed in DMF (15 mL) under nitrogen atmosphere at room temperature. After 5 min, triflate **4** (8.3 g, 23 mmol), methyl acrylate (3.0 mL, 34 mmol), and triethylamine (9.4 mL, 68 mmol) were added to the mixture successively. The mixture was heated at 100 °C for 23 h. After cooling to ca. 40 °C, the precipitate composed of salts and catalyst was filtered by Celite. Addition of distilled water to the filtrate gave a solid, which was filtered. The solid was washed with MeOH and dried under reduced pressure to give the pale yellow solid **5** (5.0 g, 72%). TLC $R_f = 0.6$ (hexane/AcOH = 2:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.67 (1H, t, $J = 1.6$ Hz), 8.36 (2H, d, $J = 1.6$ Hz), 7.75 (2H, d, $J = 16$ Hz), 6.59 (2H, d, $J = 16$ Hz), 4.43 (4H, q, $J = 7.0$ Hz), 3.83 (3H, s), 1.43 (6H, t, $J = 7.0$ Hz). mp 107−111 °C.

Methyl 3-(3,5-Diethoxycarbonylphenyl)propanoate 6. A mixture of olefin 5 (5.0 g, 16 mmol) and palladium carbon (10 wt %, 150 mg) in THF (80 mL) was stirred vigorously under hydrogen atmosphere (1 atm) at room temperature for 18 h. Palladium carbon was filtered by Celite. The filtrate was concentrated under reduced pressure to give ester **6** (5.0 g, quantitative). TLC $R_f = 0.6$ (hexane/AcOH = 2:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.53 (1H, t, $J = 1.6$ Hz, phenyl H), 8.07 (2H, d, $J = 1.6$ Hz, phenyl H), 4.40 (4H, q, $J = 7.0$ Hz, $-OCH_2CH_3$), 3.68 (3H, s, $-COOCH_3$), 3.06 (2H, t, $J = 7.8$ Hz), 2.69 (2H, t, $J = 7.8$ Hz), 1.42 (6H, t, $J = 7.0$ Hz, $-OCH_2CH_3$). mp 49−53 °C.

3-(3,5-Dihydroxymethylphenyl)propan-1-ol 7. $LiAlH_4$ (1.14 g, 24 mmol) was suspended in THF (50 mL) under nitrogen atmosphere. A solution of ester **7** (2.5 g, 8.1 mmol) in THF (25 mL) was slowly added to the suspension at 60 °C over 2 h. The mixture was heated for 3 h and then cooled to room temperature. Distilled water (1.2 mL), 12 M NaOH aqueous solution (1.2 mL), and distilled water (3.6 mL) were added at intervals of 10 min with stirring. The mixture was further stirred at 60 °C for 3 h. The mixture was dried over anhydrous $MgSO_4$, filtered by Celite, and

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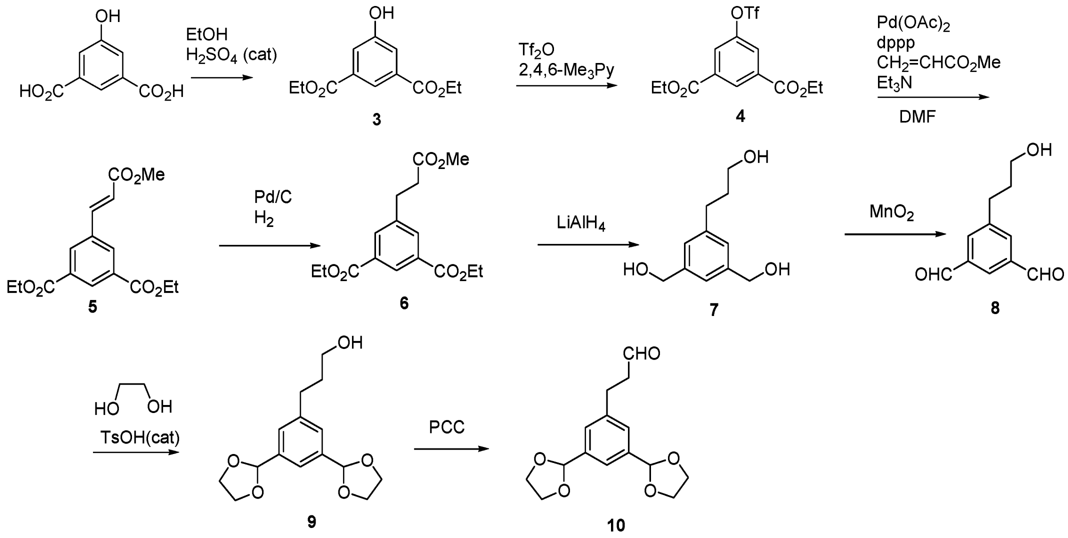
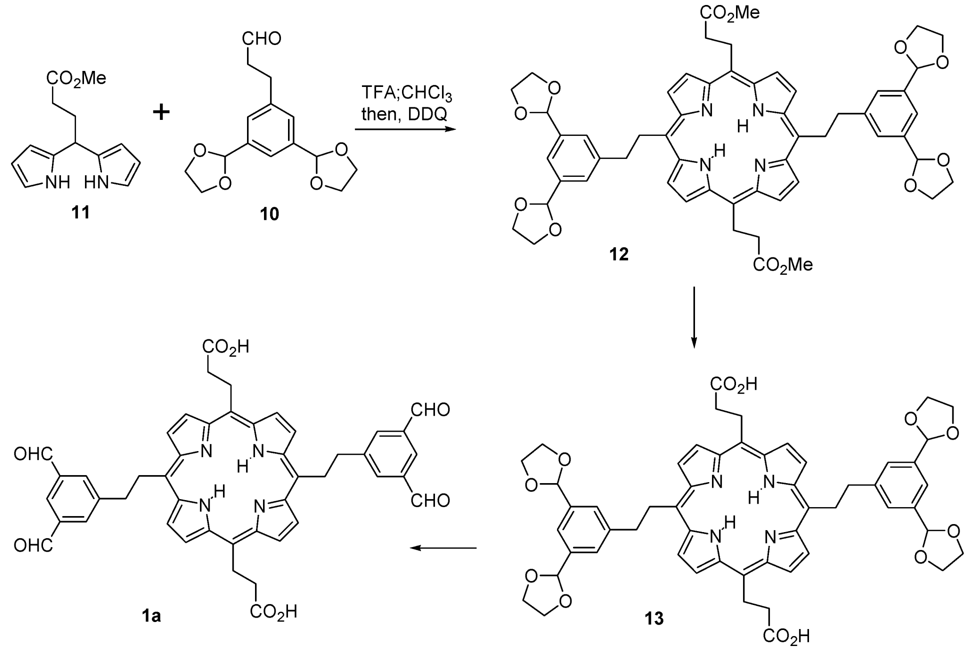
Scheme 2. Preparation of 10



Scheme 3. Preparation of Porphyrin 1a



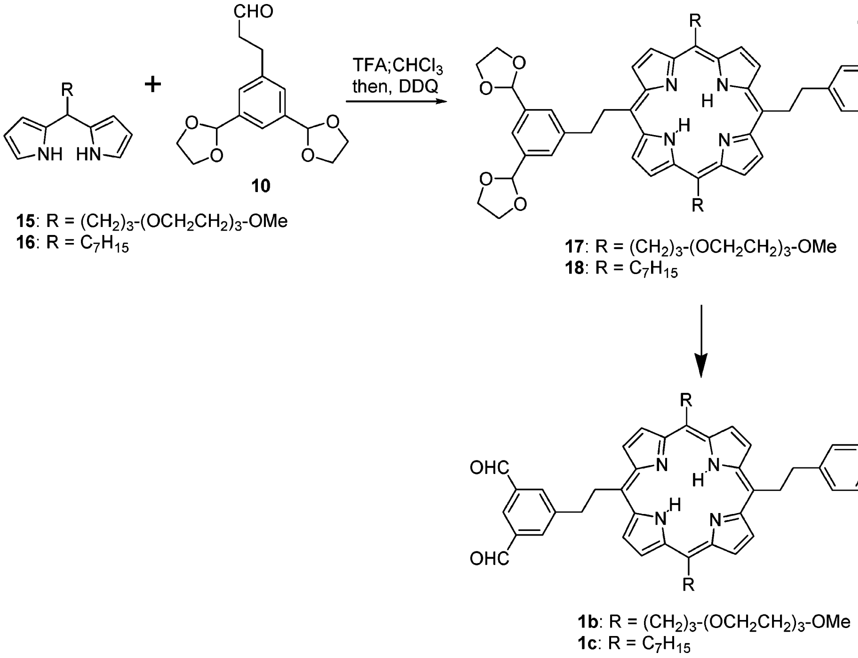
concentrated under reduced pressure to give triol **7** (1.6 g, with a small amount of THF). TLC $R_f = 0.2$ (chloroform/MeOH = 9:1). ^{1}H NMR (270 MHz, $CDCl_3$/MeOH = 1:1) δ 7.16 (1H, s, phenyl H), 7.11 (2H, s, phenyl H), 4.67 (3H, s, −OH), 4.61 (4H, s, phenyl-C*H*$_2$OH), 3.58 (2H, t, *J* = 6.5 Hz, phenyl-C*H*$_2$CH$_2$CH$_2$OH), 2.70 (2H, t, *J* = 8.1 Hz, phenyl-CH$_2$CH$_2$C*H*$_2$OH), 1.86 (2H, m, phenyl-CH$_2$C*H*$_2$CH$_2$OH).

3-(3,5-Diformylphenyl)propan-1-ol 8. MnO_2 (15 g) was added to the mixture of triol **7** (3.2 g) in THF (50 mL). The mixture was stirred at room temperature for 24 h. Manganese derivatives were filtered by Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (hexane/AcOEt = 1:1−0:1) to give dialdehyde **8** (1.53 g) and monoaldehyde (0.9 g), which was converted to dialdehyde **8** (0.62 g) by oxidation with MnO_2. Totally, dialdehyde **8** (2.15 g, 69%, two steps) was yielded as a colorless oil. TLC $R_f = 0.5$ ($CHCl_3$/MeOH = 9:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.10 (2H, s, aldehyde H), 8.21 (1H, t, *J* = 1.6 Hz, phenyl H), 8.00 (2H, d, *J* = 1.6 Hz, phenyl H), 3.70 (2H, t, *J* = 5.7 Hz, phenyl-C*H*$_2$CH$_2$-CH$_2$OH), 2.90 (2H, t, *J* = 8.1 Hz, phenyl-CH$_2$CH$_2$C*H*$_2$OH), 1.96 (2H, m, phenyl-CH$_2$C*H*$_2$CH$_2$OH).

3-{3,5-Di(1,3-dioxa-2cyclopentyl)}propan-1-ol 9. A mixture of dialdehyde **8** (2.15 g, 11.2 mmol), ethylene glycol (4 mL, 71.7 mmol), and *p*-TsOH (3 mg, catalyst) in benzene (50 mL) was heated at 100 °C for 4.5 h as water produced was removed by a Deanstark trap. The mixture was washed with saturated $NaHCO_3$ aqueous solution. The organic layer was extracted with ether, and the organic layer was washed with distilled water and brine. The mixture was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give diacetal **9** (2.6 g, 83%). TLC $R_f = 0.5$ ($CHCl_3$/MeOH = 9:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (1H, s, phenyl H), 7.33 (2H, s, phenyl H), 5.80 (2H, s, acetal H), 4.07 (8H, m, ethylene H), 3.66 (2H, t, *J* = 5.7 Hz, phenyl-C*H*$_2$CH$_2$CH$_2$OH), 2.74 (2H, t, *J* = 7.6 Hz, phenyl-CH$_2$CH$_2$C*H*$_2$OH), 1.91 (2H, m, phenyl-CH$_2$C*H*$_2$CH$_2$OH).

3-{3,5-Di(1,3-dioxa-2cyclopentyl)}propanal 10. A mixture of alcohol **9** (50 mg, 0.178 mmol), pyridinium chlorochromate (PCC, 77 mg, 0.356 mmol), sodium acetate (29 mg, 0.356 mmol), $CHCl_3$ (EtOH free, 2 mL), and molecular sieves 4A (80 mg) was stirred at room temperature for 30 min. Ether was added to the mixture, and the suspension was passed through a short column (1 cm ϕ × 5 cm height) packed with Florisil. The filtrate was concentrated

Scheme 4. Preparation of Porphyrins 1b and 1c



under reduced pressure to give aldehyde **10** (27 mg, 55%). TLC R_f = 0.65 (AcOEt). ^{1}H NMR (270 MHz, CDCl$_3$) δ 9.82 (1H, s, aldehyde H), 7.45 (1H, s, phenyl H), 7.32 (2H, s, phenyl H), 5.80 (2H, s, acetal H), 4.05 (8H, m, ethylene H), 2.99 (2H, t, J = 7.6 Hz, phenyl-C*H*$_2$CH$_2$CHO), 2.80 (2H, t, J = 7.6 Hz, phenyl-CH$_2$C*H*$_2$CHO).

5,15-Bis(methoxycarbonylethyl)-10,20-bis[2-{3,5-bis(1,3-dioxa-2-cyclopentyl)phenyl}ethyl]porphyrin 12. A 100 mL round-bottom flask was charged with aldehyde **10** (86 mg, 309 μmol), *meso*-(methoxycarbonylethyl)dipyrromethane **11**[16] (72 mg, 309 μmol), molecular sieves 4A (310 mg), and CHCl$_3$ (32 mL). After purging with N$_2$ for 10 min, TFA (12 μL, 155 μmol) was added and stirred in the dark for 24 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 140 mg, 618 μmol) was added to the mixture. After stirring for 1 h, the mixture was neutralized with triethylamine (50 μL) and concentrated under reduced pressure. The residue was purified twice by SiO$_2$ column chromatography. The tar component was removed by the first one (CHCl$_3$−10:1 CHCl$_3$/acetone); then the desired porphyrin was separated carefully by the second one (30:1 CHCl$_3$/acetone−10:1 CHCl$_3$/acetone). The collected porphyrin was sonicated in ether and washed on a membrane filter (Millipore Durapore, poly(vinylidene fluoride), 0.1 μm) with ether to give a purple solid (8.4 mg, 2.8%). TLC R_f = 0.5 (CHCl$_3$/acetone = 10:1). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.50 (8H, d, J = 4.2 Hz, pyrrole β-H), 7.67 (4H, s, phenyl H), 7.57 (2H, s, phenyl H), 5.88 (4H, s, acetal H), 5.33 (4H, t, J = 8.4 Hz), 5.23 (4H, t, J = 8.4 Hz), 4.04 (16H, m, ethylene H), 3.85 (4H, t, J = 8.4 Hz), 3.80 (6H, s, COO*Me*), 3.53 (4H, t, J = 8.4 Hz), −2.71 (2H, s, inner H). MALDI TOF mass spectra (dithranol) m/z = 979 [M]$^+$, 935 [M − OCH$_2$CH$_2$]$^+$, 891 [M − (OCH$_2$CH$_2$)$_2$]$^+$; calcd for C$_{56}$H$_{58}$N$_4$O$_{12}$ = 979.

5,15-Bis(carboxyethyl)-10,20-bis[3-{3,5-bis(1,3-dioxa-2-cyclopentyl)phenyl}ethyl]porphyrin 13. A mixture of ester **12** (4.8 mg, 4.9 μmol) and 8 M NaOH/MeOH/THF = 2:4:7 (v/v) (4 mL) was stirred at room temperature under nitrogen atmosphere for 45 min. The pH was adjusted to 6 with acetic acid. Distilled water (5 mL) was added to the mixture, and the organic layer was extracted with CHCl$_3$/MeOH (2:1). After evaporation, distilled water (5 mL) was added, and the mixture was sonicated. Precipitate was washed with water on a membrane filter (Millipore Durapore, poly(vinylidene fluoride), 0.1 μm). The precipitate was once dissolved in a mixture of CHCl$_3$/MeOH/AcOH (3 mL:1 mL:5 drops) and then evaporated. The residual solid was sonicated in CHCl$_3$ and washed with CHCl$_3$ on a membrane filter (Millipore Durapore, poly(vinylidene fluoride), 0.1 μm) to give acid **13** (4.1 mg, 88%). The solid can be dissolved in a mixture of CHCl$_3$/MeOH/AcOH (3 mL:1 mL:5 drops). TLC R_f = 0.4 (CHCl$_3$/acetone = 1:1). MALDI TOF mass spectra (dithranol) m/z = 952 [M + H]$^+$, 908 [M − OCH$_2$CH$_2$]$^+$, 715 [M − (OCH$_2$CH$_2$)$_2$]$^+$; calcd for C$_{56}$H$_{58}$N$_4$O$_{12}$ = 951.

5,15-Bis(carboxyethyl)-10,20-bis{2-(3,5-diformylphenyl)ethyl}-porphyrin 14. Acetal **13** was dissolved in a mixture of THF (3 mL) and 3 M HCl (1.5 mL) and stirred under nitrogen atmosphere at room temperature for 30 min. The mixture was cooled to 0 °C. The pH was adjusted to 6 with 3 M NaOH and acetic acid. CHCl$_3$ (5 mL) and distilled water (5 mL) were added to the mixture, and the mixture was mixed vigorously. A water layer was removed by a pipet, and the CHCl$_3$ layer was evaporated. Residue was sonicated in water, and washed with water on a membrane filter (Millipore Fluoropore, PTFE, 0.2 μm). The solid was reprecipitated from DMF/ether, and the precipitate was washed with ether. These reprecipitation and washing procedures were repeated twice to give a purple solid (3.0 mg, 90%). TLC R_f = 0.35 (CHCl$_3$/acetone (10:1) 5 mL + AcOH (1 drop)), ^{1}H NMR (600 MHz, pyridine-d_5) δ 10.18 (4H, s, C*H*O), 9.88 (4H, d, J = 3.8 Hz, pyrrole β-H), 9.76 (4H, d, J = 3.8 Hz, pyrrole β-H), 8.49 (2H, s, phenyl H), 8.40 (4H, s, phenyl H), 5.67 (4H, t, J = 8.2 Hz), 5.43 (4H, t, J = 8.2 Hz), 4.02 (4H, t, J = 8.2 Hz), 3.88 (4H, t, J = 8.2 Hz), −2.12 (2H, s, inner H). MALDI TOF mass spectra (dithranol) m/z = 775 [M$^+$], 628 [M − CH$_2$C$_6$H$_3$(CHO)$_2$]$^+$, 854 [M − CH$_2$C$_6$H$_3$(CHO)$_2$ + dithranol]$^+$, 1001 [M + dithranol]$^+$, 1228 [M + (dithranol)$_2$]$^+$, 1456 [M + (dithranol)$_3$]$^+$; calcd for C$_{56}$H$_{58}$N$_4$O$_{12}$ = 775. UV−vis (pyridine) $\lambda_{\max}$/nm (absorbance): 421 (0.599, ϵ 1.4 × 10^5 mol^{-1} cm^{-1}), 521 (0.029), 555 (0.017), 601 (0.009), 659 (0.010). Fluorescence (pyridine, λ_{EX}: 421 nm, absorbance = 0.0849) λ_{EM}/nm (intensity):661 (210), 733 (70).

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***meso*-Methoxyethoxyethoxyethoxypropyldipyrromethane 15.** A 100 mL round-bottom flask was charged with 4-(methoxyethoxyethoxyethoxy)butanal (0.9 g, 3.84 mmol) and pyrrole (10.5 mL, 153 mmol). After purging with N_2 for 2 min, TFA (29 μL, 0.384 mmol) was added and the mixture was stirred in the dark for 2.5 h. Saturated $NaHCO_3$ was added to the mixture. The organic layer was extracted with $CHCl_3$ and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (EtOAc/hexane 50−80%) to give dipyrromethane **15**[16] (0.79 g, 59%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.35 (br, 2H, NH), 6.64−6.61 (m, 2H, pyrrole 5), 6.13−6.08 (m, 2H, pyrrole 4), 6.02−5.97 (m, 2H, pyrrole 3), 4.11 (t, $J = 8.1$ Hz, 1H, CH), 3.68−3.44 (m, 14H, CH_2O), 3.32 (s, 3H, MeO), 2.12−2.01 (m, 2H, CH_2), 1.65−1.55 (m, 2H, CH_2).

5,15-Bis(methoxyethoxyethoxyethoxypropyl)-10,20-[3-{3,5-bis(1,3-dioxa-2-cyclopentyl)phenyl}ethyl]porphyrin 17. A 50 mL round-bottom flask was charged with aldehyde **10** (50 mg, 180 μmol), dipyrromethane **15** (63 mg, 180 μmol), molecular sieves 4A (100 mg), and $CHCl_3$ (18 mL). After purging with N_2 for 10 min, TFA (7 μL, 90 μmol) was added and the mixture was stirred in the dark for 2 h. DDQ (82 mg, 0.36 mmol) was added to the mixture. After stirring for 2 h, the mixture was neutralized with triethylamine (0.2 mL) and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography to give porphyrin **17** (10 mg, 9%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (d, $J = 4.4$ Hz, 4H, β pyrrole), 9.51 (d, $J = 4.4$ Hz, 4H, β pyrrole), 7.64 (s, 4H, Ar), 7.57 (s, 2H, Ar), 5.91 (s, 4H, O−CH−O), 5.30−5.24 (m, 4H), 5.12−5.06 (m, 4H), 4.14−3.33 (m, 54H), 2.82−2.78 (m, 4H), −2.65 (s, 2H, NH).

5,15-Bis(methoxyethoxyethoxyethoxypropyl)-10,20-[3-{3,5-bis(1,3-formyl)phenyl}ethyl]porphyrin 1b. Hydrolysis of acetal **17** (10 mg) was carried out according to the procedure for synthesis of **1a**. Purification by SiO_2 column chromatography (2-propanol/EtOAc, 5−10%) gave **1b** (2.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 4H, CHO), 9.57 (d, $J = 4.4$ Hz, β pyrrole), 9.41 (d, $J = 4.4$ Hz, β pyrrole), 8.26 (s, 2H, Ar). 8.06 (s, 2H, Ar), 5.30 (t, 4H, $J = 8.0$ Hz, CH_2), 5.08 (t, 4H, $J = 8.0$ Hz, CH_2), 3.95 (t, 4H, $J = 8.0$ Hz, CH_2), 3.88−3.82 (m, 8H), 3.78−3.71 (m, 12H), 3.69−3.67 (m, 4H), 3.56−3.52 (m, 4H), 3.33 (s, 6H, MeO), 2.82−2.76 (m, 4H), −3.3 (s).

5,15-Bisheptyl-10,20-[3-{3,5-bis(1,3-dioxa-2-cyclopentyl)phenyl}ethyl]porphyrin 18. A 50 mL round-bottom flask was charged with aldehyde **10** (78 mg, 280 μmol), *meso*-heptyldipyrromethane **16**[17] (69 mg, 280 μmol), molecular sieves 4A (200 mg), and $CHCl_3$ (28 mL). After purging with N_2 for 10 min, TFA (10 μL, 140 μmol) was added and the mixture was stirred in the dark for 3 h. DDQ (127 mg, 0.56 mmol) was added to the mixture. After stirring for 4 h, the mixture was neutralized with triethylamine (0.2 mL) and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography to give porphyrin **18** (9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 8H, β pyrrole), 7.68 (s, 4H, Ar), 7.60 (s, 2H, Ar), 5.94 (s, 4H, O−CH−O), 5.29 (m, 4H, CH_2), 4.97 (m, 4H, CH_2), 4.10−4.02 (m, 16H, O−CH_2), 3.89 (m, 4H, CH_2), 2.55 (m, 4H, CH_2), 1.84 (m, 4H, CH_2), 1.56 (m, 4H, CH_2), 1.40 (m, 8H, CH_2), 0.95 (m, 6H), −2.6 (s, 2H, NH).

5,15-Bisheptyl-10,20-[3-{3,5-bis(1,3-formyl)phenyl}ethyl]porphyrin 1c. Hydrolysis of acetal **18** (9 mg) was carried out according to the procedure for the synthesis of **1a**. Purification by SiO_2 column chromatography (EtOAc/hexane, 20−30−100%) gave **1c** (9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 4H, CHO), 9.48 (d, 4H, $J = 4.4$ Hz, β pyrrole), 9.38 (d, 4H, $J = 4.4$ Hz, β pyrrole), 8.25 (s, 4H, Ar), 8.05 (s, 8H, Ar), 5.26 (m, 4H, CH_2), 4.94 (m, 4H, CH_2), 3.89 (m, 4H, CH_2), 2.52 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 1.55 (m, 4H, CH_2), 1.39 (m, 8H, CH_2), 0.93 (m, 6H, CH_3), −2.70 (s, 2H, NH).

Modified SWNTs were prepared according to the reported procedure (ref 18). Suspension of SWNTs (tube@rice, 10 mL in H_2O with surfactant) and HNO_3 solution (5 M, 20 mL) was heated at 110 °C for 1 h. The reaction mixture was filtered by a membrane filter (Millipore Isopore, polycarbonate, 0.1 μm), and the black thin solid was washed with distilled water on the filter. The solid was dried under reduced pressure. A mixture of the solid and octadecylamine (2 g) was set in a test tube with a screw cap and heated at 130 °C under nitrogen for 6 days. To remove excess octadecylamine, hot EtOH was added to the mixture, and the mixture was filtered by a membrane filter (Millipore Isopore, polycarbonate, 0.1 μm). This procedure was repeated until white solid (octadecylamine) disappeared. A black thin film was dried under reduced pressure to give modified SWNTs (58.5 mg). Modified SWNTs (3.4 mg) were dispersed in *o*-$C_6H_4Cl_2$ (6 mL), and the solution was used as an SWNT stock solution.

Preparation of Porphyrin/SWNT Composite. Stock solutions were prepared as follows: Solution **1a** in pyridine (1.3 mM); solution **1b** and **1c** in $CHCl_3$ (1.3 mM); solution **2a** and **2b** in EtOH (2.6 mM); solution **2c** in EtOH (5.2 mM); solution SWNTs in *o*-$C_6H_4Cl_2$ (modified CNT 0.57 mg/mL).

A mixture of modified SWNTs (0.2 mL of solution SWNTs, 113 μg) and porphyrin (0.25 mL of solution **1a**, **1b**, or **1c**, 0.33 μmol) in EtOH (3 mL) was sonicated for 2 min. Aminopyrene (0.25 mL of solution **2a**, **2b**, or **2c**, 0.66 μmol for **2a** and **2b**, 1.3 μmol for **2c**) and EtOH (1 mL) were added to the mixture. The mixture was sonicated for 30 s and heated at 75 °C for 4 h. EtOH (5 mL) was added to the mixture, and the mixture was filtered on a membrane filter (Millipore Durapore, poly(vinylidene fluoride), 0.1 μm). Free porphyrin and aminopyrene were thoroughly washed with $CHCl_3$ (15 mL), MeOH (15 mL), and EtOH (15 mL) on the membrane filter. The CNT composite remaining on the filter was immediately peeled from the filter and dispersed by sonication in $CHCl_3$ (10 mL) with a trace amount of pyridine (3 drops). A part of the dispersed solution was diluted 4-fold and used for the measurements of absorption and fluorescence spectra in solution. Composites without aminopyrenes were obtained by the same manner in the absence of aminopyrene.

Detachment of Porphyrin from Composites. Composite solution (1 mL) was added to a solution of MeOH (2.5 mL) and 4.5 M HCl (1 mL). The mixture was stirred under nitrogen atmosphere at room temperature for 1 h. The mixture was neutralized with 10 M NaOH (0.4 mL) and $NaHCO_3$ aqueous solution. The organic layer was extracted with $CHCl_3$ and evaporated under reduced pressure. All residues were dissolved in DMF (3 mL), and the amount of porphyrin was analyzed by UV−vis spectroscopy. Extinction coefficients (**1a**, $\epsilon_{421\,\mathrm{nm}} = 1.4 \times 10^5$ M^{-1} cm^{-1}; **1b**, $\epsilon_{421\,\mathrm{nm}} = 3.8 \times 10^5$ M^{-1} cm^{-1}; **1c**, $\epsilon_{421\,\mathrm{nm}} = 3.5 \times 10^5$ M^{-1} cm^{-1}) were used for the analysis.

Results and Discussion

To isolate porphyrin/CNT composites, we prepared tetraformylporphyrins **1a**, **1b**, and **1c** and aminopyrenes **2a**, **2b**, and **2c**. Two isophthalaldehyde groups were attached to porphyrin **1** for imine polymerization with diaminopyrenes (Scheme 5). Other substituents, namely carboxylic acid (**1a**), oligoether (**1b**), and alkyl groups (**1c**), were selected to compare the effect of functional groups. Since both porphyrin and pyrene are known to interact with CNTs,[10,13] condensa-

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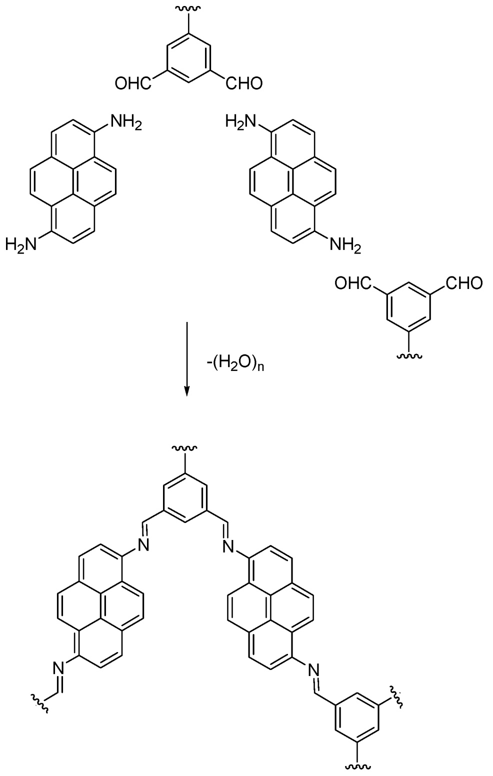
[17] Tomohiro, Y.; Satake, A.; Kobuke, Y. *J. Org. Chem.* **2001**, *66*, 8442−8446.

Scheme 5. Expected Imine Formation by Tetraformylporphyrin 1 and Diaminopyrene 2a



tion of tetraformylporphyrins and diaminopyrenes on the surface of the CNT is expected to proceed, causing it to become wrapped by an imine polymer. We used single-walled CNTs (SWNTs) prepared by laser ablation. The mean tube diameter of the SWNTs was 1.2 nm. To disperse the SWNTs in common organic solvents such as $CHCl_3$, the purified SWNTs were modified by zwitterion formation with octadecylamine using a technique described in the ref 18. The near-IR and Raman spectra of the modified SWNTs on a quartz glass were identical to those of the as-purchased product, showing that no side-wall oxidation had occurred. The porphyrin/SWNT composite was prepared by stirring the modified SWNTs (113 μg) and porphyrin **1a**−**c** (0.33 μmol) with or without aminopyrene **2a**−**c** (0.66 μmol for **2a**,**b**, 1.3 μmol for **2c**) in EtOH (4 mL) at 75 °C for 4 h. The reaction mixture was filtered using a membrane filter, and free porphyrin and aminopyrene were washed successively with $CHCl_3$, MeOH, and EtOH. The SWNT composite that remained on the filter was immediately peeled off from the filter and dispersed by sonication in $CHCl_3$ with a trace amount of pyridine. The dispersed solution was diluted and used for absorption and fluorescence measurements. In what follows, the composites will be referred to by the codes corresponding to the compounds used, e.g., **1a**-**2a**-SWNTs and **1a**-SWNTs. Imine bond formation was observed in the IR spectrum at 1650 cm^{-1} (C═N) in the case of **1b**-**2a**-SWNTs, and the peak corresponding to the aldehyde C═O bond (1697 cm^{-1}) was barely visible (Figure 1) Although it was difficult to observe the stretching signal of imine in **1a**-**2a**-SWNTs and **1a**-**2b**-SWNTs because of overlapping with the strong C(O)O signal of carboxylic acid, the C═O signal corresponding to aldehyde disappeared, which indicated the formation of the imine bond.

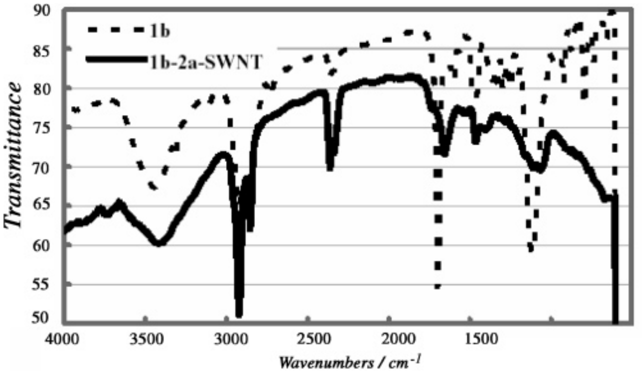


Figure 1. IR spectra (KBr) of porphyrin **1b** (dotted line) and CNT composite **1b**-**2a**-SWNTs (solid line).

Absorption spectra of **1a**-**2a**-SWNTs and uncoated SWNTs on quartz glass plates are shown in Figure 2A. The spectra are virtually identical in the 800−2500 nm range. Thus, the characteristic semiconducting bands I (SI) and II (SII) of SWNTs around 1600 and 900 nm, respectively, remain unperturbed even after composite formation. On the other hand, a unique absorption peak corresponding to the Soret band of porphyrin was observed at 420 nm in the composite. Similar UV−vis−near-IR spectra were obtained in other polymer-wrapped composites, namely **1a**-**2b**-SWNTs, **1b**-**2a**-SWNTs, and the non-pyrene composite **1a**-SWNTs (not shown). In all cases, the intrinsic SI and SII bands of SWNTs were uninfluenced by composite formation. Resonance Raman signals corresponding to the composite's radial breathing mode (RBM) around 100−350 cm^{-1} and the G-line at 1590 cm^{-1} were also the same as those of pure SWNTs (Figure S1 in the Supporting Information). By contrast, the absorption spectra of the porphyrin part changed significantly. UV−vis spectra of homogeneous solutions of **1a**-**2a**-SWNTs and **1a**-SWNTs, and **1a** in $CHCl_3$, are shown in Figure 2B. Broad Soret bands were observed in both **1a**-**2a**-SWNTs and **1a**-SWNTs, their peak maxima red shifting to 425 and 421 nm, respectively, while that of **1a** occurred at 420 nm. The difference between **1a**-**2a**-SWNTs and **1a**-SWNTs was clearly visible in the Q-band region. The four characteristic Q-bands (518, 551, 599, and 656 nm for **1a**) of free-base porphyrin were observed with small red shifts in **1a**-SWNTs (524, 559, 602, and 659 nm), while the Q-bands of **1a**-**2a**-SWNTs exhibited markedly lower intensities. The absorption spectrum of the reference polymer prepared from **1a** and **2a** (Figure S2 in the Supporting Information) showed clear Q-bands, suggesting that the significant decrease in Q-band intensity in **1a**-**2a**-SWNTs is caused by the interaction between porphyrin and SWNTs. No distinct absorption peak corresponding to the pyrene moiety was observed for **1a**-**2a**-SWNTs. UV−vis spectra of other composites are shown in Figure S3 in the Supporting Information. Broad Soret and Q-bands similar to those of **1a**-**2a**-SWNTs were observed for **1a**-**2b**-SWNTs and **1a**-**2c**-SWNTs as well. Relatively sharp Soret and Q-bands were observed in the case of **1b**- and **1c**-diaminopyrene-SWNTs

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(18) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.

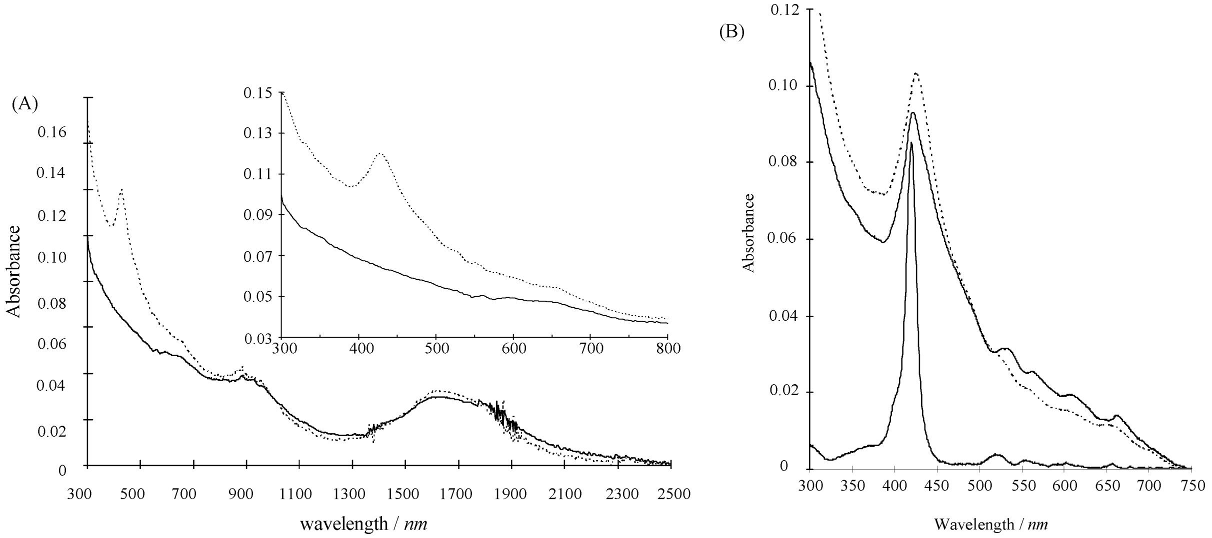

Figure 2. (A) UV−vis−near-IR spectra of **1a**-**2a**-SWNTs (dotted line) and only SWNTs (solid line) on a quartz glass. (B) UV−vis spectra normalized to zero absorption at 750 nm of **1a**-**2a**-SWNTs (dotted line), **1a**-SWNTs (upper solid line), and **1a** (lower solid line) in $CHCl_3$.

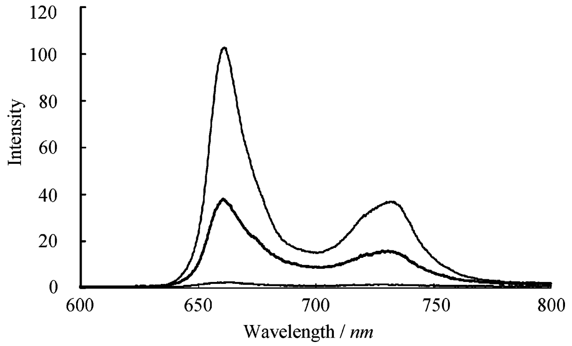

Figure 3. Fluorescence spectra of **1a** (top), **1a**-SWNTs (middle), and **1a**-**2a**-SWNTs (bottom) in $CHCl_3$ excited at Soret bands normalized to absorbance 0.1 for the porphyrin moiety. The contribution of SWNTs was subtracted.

as compared with **1a**-**2a**-SWNTs, whereas these bands were scarcely observed in **1b**-SWNTs, **1c**-SWNTs, **1b**-**2c**-SWNTs, and **1c**-**2c**-SWNTs. These results indicate that polymer wrapping using diaminopyrene **2a** or **2b** is a useful approach to ensuring that substantial amounts of **1a**−**c** interact strongly with SWNTs.

Fluorescence spectra of **1a**-SWNTs, **1a**-**2a**-SWNTs, and free-base **1a** were compared (Figure 3). The spectra are of samples having the same absorbance (0.1 at the Soret band of the porphyrin moiety; the contribution of SWNTs was subtracted) at the excitation wavelength. The fluorescence intensity from the porphyrin part decreased to 37% and 2% of that of **1a** in **1a**-SWNTs and **1a**-**2a**-SWNTs, respectively.[19] Since excitation/emission spectra of **1a**-SWNTs and **1a**-**2a**-SWNTs were similar to those of **1a**, the fluorescent component in the composites presumably came from free porphyrin and/or porphyrin weakly interacting with SWNTs. Although the Soret band absorptions of **1a**-SWNTs and **1a**-**2a**-SWNTs are similar in UV−vis spectra (Figure 2B), the quenching of **1a**-SWNTs is much less efficient. This suggests that the polymer-wrapping procedure using diaminopyrenes is important in enabling a strong interaction with SWNTs.

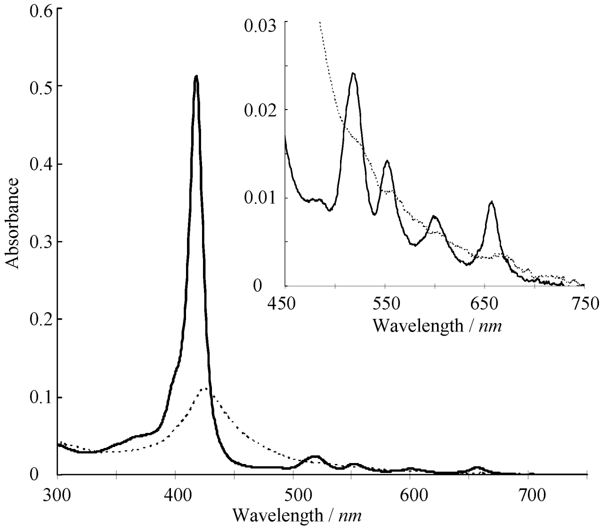

Figure 4. UV−vis spectrum of porphyrin parts peeled off from composite **1a**-**2a**-SWNTs (solid line) and a difference spectrum subtracting the corresponding SWNT part from the spectrum of **1a**-**2a**-SWNTs (dotted line). Inset: enlarged spectra of Q-band parts.

The quenching efficiency of the polymer-wrapping composites tested followed decreasing order: 98% (**1a**-**2a**-SWNTs), 97% (**1a**-**2b**-SWNTs), 97% (**1b**-**2a**-SWNTs), 89% (**1b**-**2b**-SWNTs), 88% (**1c**-**2a**-SWNTs), and 81% (**1c**-**2b**-SWNTs). This suggests the relative order **1a** > **1b** > **1c** for the porphyrin part and **2a** > **2b** for the pyrene part.

To estimate the amount of porphyrin in the composites, acid hydrolysis was carried out. This procedure removed porphyrin derivatives not only from imine composites, such as **1a**-**2a**-SWNTs and **1a**-**2b**-SWNTs, but also from **1a**-SWNTs. Peeled-off porphyrin was recovered, and the amount was determined from the absorption spectrum, which was identical to the original spectrum of **1a**. Figure 4 shows the absorption spectrum of the peeled-off porphyrin from **1a**-**2a**-SWNTs and the difference spectrum obtained by subtracting that of SWNTs normalized at 750 nm from that of **1a**-**2a**-SWNTs. The two spectra were obtained using the same amount of the identical composite. The figure indicates that, in the case of the composite, the extinction coefficient

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(19) The fluorescence intensity of **1a**−**2c** is almost same as that of **1a** (96% compared with **1a**).

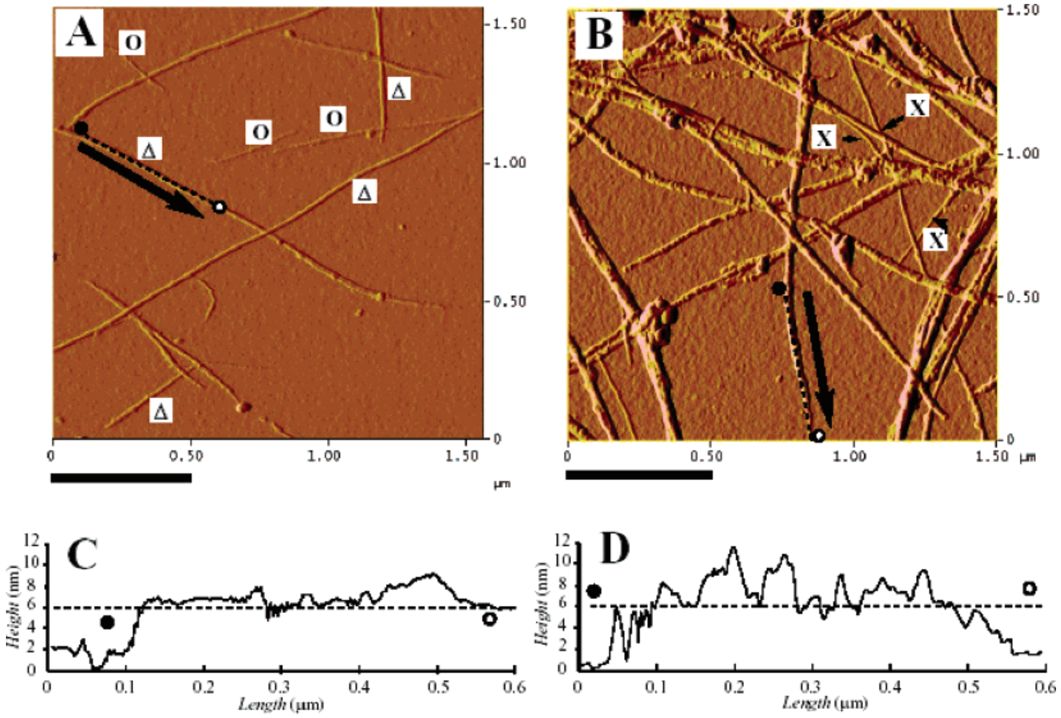

Figure 5. AFM images of (A) SWNTs and (B) **1a**-**2a**-SWNTs composite. Scale bar 500 nm. "○" and "△" in (A) indicate nanotubes of 1.5−2.0 and 4−6 nm heights, respectively. "X" in (B) indicates the smooth part in heterogeneous composite mixtures. Cross sections of (C) SWNTs and (D) **1a**-**2a**-SWNTs along the tube axis from filled to open circles, as shown by arrows in (A) and (B).

of the Soret band decreased to about 20%, accompanied by a red shift of 5 nm. This behavior resembles the interaction between porphyrin and C_{60},[20] indicating that the hypochromic and red shifts of the Soret band are commonly induced by interacting with π-conjugated carbon materials. The decreases observed in the apparent extinction coefficient at the Soret band were 21% (**1a**-**2a**-SWNTs), 19% (**1a**-**2b**-SWNTs), 21% (**1a**-SWNTs), 33% (**1b**-**2a**-SWNTs), 25% (**1b**-**2b**-SWNTs), 33% (**1c**-**2a**-SWNTs), and 48% (**1c**-**2b**-SWNTs). This suggests that the strength of the interaction with SWNTs decreased in the order **1a** > **1b** > **1c**, which agreed with the degree of fluorescence quenching.

Amounts of porphyrin bound in SWNT composites (1 mg) were determined by UV−vis absorption spectra of peeled-off porphyrins. The results are tabulated in Table 1. A comparison between the amounts of **1a**, **1b**, and **1c** in their respective composites (runs 1, 2, 4, 5, 8, and 9) revealed that **1a** was 1.8−6.5-fold more abundant than **1b** and **1c**. The fact that **1a** shows a high affinity with SWNTs in the absence of diaminopyrene (**1a**-SWNTs) suggests that the carboxylic acid group may play an important role in the composite formation reaction.

To examine the nature of interaction in the composite, AFM and HRTEM images were taken. AFM images of SWNTs and **1a**-**2a**-SWNTs on SiO_2/Si substrates, and their cross-sectional profiles, are shown in Figure 5. Uncoated SWNTs samples had highly smooth surfaces, and their heights were classifiable into two ranges, namely 1.5−2.0 nm (indicated by the open circles in Figure 5A) and 4−6 nm (indicated by open triangles), showing that SWNT samples contain both individual and bundle tubes. By contrast, the **1a**-**2a**-SWNTs sample exhibited heterogeneous distributions containing relatively aggregated tubes. In the case of **1a**-**2a**-SWNTs, rough outer surfaces typically 4−6 nm in height were observed (Figure 5D), along with smooth sections (indicated by X's in Figure 5B), which presumably represent the naked SWNTs.

Table 1. Amounts of Porphyrin Interacted with SWNTs (1 mg)[a]

run	sample	porphyrin (μmol)
1	**1a**-**2a**-SWNTs	1.3
2	**1a**-**2b**-SWNTs	1.1
3	**1a**-SWNTs	0.78
4	**1b**-**2a**-SWNTs	0.21
5	**1b**-**2b**-SWNTs	0.17
6	**1b**-**2c**-SWNTs	0.024
7	**1b**-SWNTs	<0.007
8	**1c**-**2a**-SWNTs	0.73
9	**1c**-**2b**-SWNTs	0.44
10	**1c**-**2c**-SWNTs	0.033
11	**1c**-SWNTs	0.019

[a] Determined by absorption spectra of peeled-off porphyrin from composites.

A HRTEM image of **1a**-**2b**-SWNTs is shown in Figure 6A. Two separate bundles were placed as indicated by the two arrows. The material wrapping the nanotube bundles (shown in red in Figure 6B) shaded the striped images. The contrast of this wrapping material is the same as that of SWNTs, indicating that it must be organic material. The material seems to be rolling up around SWNT bundles, resulting in the rough surface profiles observed.

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[20] (a) Tashiro, K.; Aida, T.; Zheng, J.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477. (b) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704. (c) Kimura, M.; Shiba, T.; Yamazaki, M.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc.* **2001**, *123*, 5636. (d) Kubo, Y.; Sugasaki, A.; Ikeda, M.; Sugiyasu, K.; Sonoda, K.; Ikeda, A.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2002**, *4*, 925.

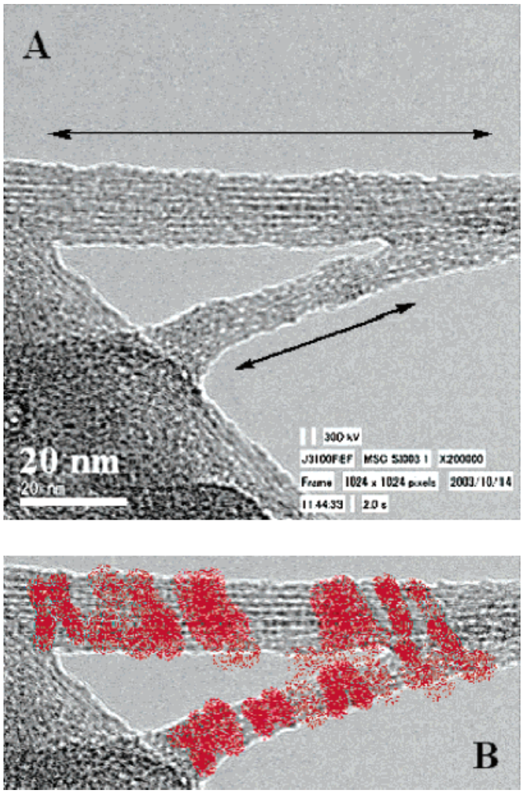

Figure 6. (A) HRTEM image of **1a**-**2b**-SWNTs composite deposited on a micromesh grid. Scale bar 20 nm. (B) Modified image of (A). Wrapping materials around nanotube bundles are emphasized by red color.

Conclusion

We succeeded in synthesizing stable porphyrin/diaminopyrene/SWNT composites by a noncovalent wrapping approach. The degree of interaction between SWNTs and porphyrin was evaluated by UV−vis and fluorescence spectra and the amount of porphyrin stripped off from the components. Substituents at two meso positions affected the amounts of porphyrin bound in with SWNT composites. Porphyrins containing carboxylic acids (**1a**) showed a higher affinity than those containing oligoether (**1b**) or alkyl (**1c**) groups. In the high-affinity combinations **1a**-**2a**-SWNTs and **1a**-**2b**-SWNTs, Soret and Q-bands were significantly broadened and their fluorescence was almost completely quenched. Apparent extinction coefficients at the Soret bands of the porphyrin moiety in the composites were reduced to ca. 20%. The present study represents the first spectral analysis of porphyrins deposited by intermolecular forces on carbon nanotubes. The results obtained will form an important basis for characterization of porphyrin/SWNT composites as well as other types of SWNT composites.

Acknowledgment. We thank Ms. Haruta and Mr. Takeuchi for AFM measurements, and Mr. Furusho for TEM measurements. This work was partially supported by the CREST (Core Research for Evolutional Science and Technology) program from JST (Japan Science and Technology Agency) and a Grant-in-Aid for Scientific Research (A) (15205020) from the Ministry of Education, Science, Sports and Culture.

Supporting Information Available: Raman spectra of SWNTs and **1a**-**2b**-SWNTs, UV−vis spectra of the reference polymer (prepared from **1a** and **2a**) and **1**-**2**-SWNT composites. This material is available free of charge via the Internet at http://pubs.acs.org.

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