

Coral reef-like functionalized self-assembled monolayers for network formation of carbon nanotube with diameter selectivity

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ABSTRACT

Despite the many advances that have been made in using anionic surfactants to disperse and sort single-walled carbon nanotubes (SWNTs) for optoelectronic applications, one-pot methods for deposition of SWNTs in a diameter (d_t) and position controlled manner from as-dispersed sample are essential. Here, we designed and prepared flavin-containing self-assembled monolayers (flavin-SAMs) that can be used to assemble d_t -selective individualized SWNT networks directly from SWNT dispersions by using the widely-used anionic surfactant. For a given glass substrate, the dimethylsilyl-linked azide, along with surface immobilization was employed to have Click reaction with terminal acetylene tethered to flavin group known to have strong affinity with SWNT. As demonstrated by atomic force microscopy and other methods, along successful assembly of individualized networks, the SWNTs are either fully or partially wrapped in a d_t selective manner by isoalloxazine moieties tethered to the surface, displaying Langmuir isotherm adsorption behaviors in a dipping method dependent manner. The assembled SWNT network secures photoluminescence and electrical conductivity albeit its intimacy to underlying substrate and near monolayer coverage of SWNT network, respectively, and, furthermore, preferentially takes place on flavin-SAM over hydrophobic surface.

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1. Introduction

Single-walled carbon nanotubes (SWNTs) are seamless hollow cylindrical rolls of graphene that have a chiral index (n, m) [1,2]. These materials possess excellent electrical properties including high carrier mobility and conductivity [3,4], and in the case of semiconducting (*sem*) nanotubes, they have diameter (d_t)-dependent band gaps according to chiral vector (n, m) [5–7]. Optoelectronic applications of SWNTs, for example as field-effect transistors [3,8–12], photovoltaics [13–15], and transparent conductive films [16,17], hinges on their ability to form thin film [18,19] that can be utilized from dispersion [20]. Because electronic performances of thin films are highly dependent on the aggregation states and uniformity of surface SWNTs, it is especially important to create individualized SWNT network structures on a given substrate. Especially, in SWNT bundles, electrical current only flows on the outermost tubes and inner tubes do not significantly contribute to the current [21]. Thus, bundling results in large off-current in a

SWNT based thin film transistor, leading to high power consumption [9,22]. Moreover, SWNT bundling produces heterogeneity of electronic types owing to co-existence of metallic (*met*) and *sem*-SWNTs.

Owing to this issue, an enormous effort has been given during the past decades to the development of protocols for dispersion of individualized SWNTs that use surfactants and aqueous solutions [23–25]. As compared to those in neat organic solvents, surfactant-based aqueous dispersions have several advantages. Firstly, aqueous surfactant systems are environmentally benign and they support high concentrations of the SWNTs. Although neat polar solvents such as *N*-methylpyrrolidone can be utilized to disperse individualized SWNTs [26] but only small quantity (*i.e.*, 0.1 mg/mL), which is much lower than the commonly required >1 mg/mL value needed for industrial applications [18]. Secondly, various surfactant-based aqueous dispersions have been utilized to separate SWNTs into single electronic type and band gaps [12,27–30] needed for high-end applications.

Although charges on ionic surfactants surrounding individualized SWNTs are beneficial for attainment of high aqueous dispersibilities and homogeneous optoelectronic properties, they lead to inhomogeneous SWNT deposition on a desired substrate and,

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sometimes, even to no assembly as a result of Coulombic repulsion between ionic head groups of the surfactants placed on nano-materials and substrate [10,27,31]. Therefore, SWNTs wrapped by anionic surfactants often require either co-use of adhesion promoters such as divalent metals (e.g., MgCl_2 [27]) or transfer method of already made SWNT thin film to a desired substrate [20]. In this event, nonionic surfactants such as Triton X-100 form more uniform films on polymeric substrates compared to anionic surfactants including the most widely used sodium dodecyl sulfate (SDS) [31]. More recently, Javey and co-workers [10] found that steroid-based surfactants form self-assembled monolayers (SAMs) that promote deposition of SWNT by hydrophobic interactions. Those evidences necessitate stable and secure method to assembly SWNT in controlled manner.

These results indicate that surface functionality on substrate must be precisely designed in order to maximize assembly of SWNT dispersions [6,7]. In this regard, owing to its profound affinity (2 eV) [32] for graphene sidewalls flavin moiety (orange chemical structure in Fig. 1a) in flavin mononucleotide (FMN) [33] and its analogues [34,35] have been utilized to disperse individualized SWNTs [25,26,35]. For instance, FMN stabilizes SWNT dispersions through three major forces [34] including i) π - π interactions between the FMN isoalloxazine ring and graphene sidewalls, ii) hydrogen bonding between the isoalloxazine moieties that produces helical assemblies, iii) solvent interactions of the FMN terminal ribityl phosphate group. The specific affinities of flavin derivatives and resulting helical assemblies can be employed advantageously to preferentially form (or sort) SWNTs having one chirality [34,36],

electronic type [12] and handedness [37]. Importantly, π - π interactions between isoalloxazine moieties-SWNT are much stronger than hydrophobic interaction between SDS-SWNT entities [38,39]. As a result, FMN and its analogues can potentially be incorporated into novel functional SAMs to enhance assembly of anionic surfactant dispersed SWNTs. The viability of this approach is inferred by the observation of precipitation-less replacement by FMN of SDS in dispersed SWNTs [38]. Of course, it would be more desirable to utilize the alternative approach mentioned above that employ FMN functionalized SAMs for selective immobilization of SWNTs according to physical properties.

In the investigation described below, we prepared novel flavin-tethered SAMs that are capable of assembling individualized SWNT networks directly from a SDS dispersion, like coral reef. The flavin-SAMs were prepared by using sequences in which the timing of steps differs, but all involve key Click reactions and begin with a flavin-linked acetylene and a dimethylsilyl terminated azide. The flavin-SAMs were quantitatively characterized by employing elemental analysis, absorption, and Fourier transform (FT) infrared (IR) spectroscopies. Importantly, immersion of the flavin-SAMs in mixtures containing aqueous a SDS-dispersed SWNT leads to formation of individualized SWNT assemblies, evident by profound photoluminescence (PL). Formation of the surface assemblies displays Langmuir isotherm kinetics and an apparent rate constant for sonication-assisted deposition of the SWNT is ten times larger than that for simple dipping. The results of atomic (AFM) and electrostatic (EFM) force microscope measurements demonstrate that the SWNTs produced in this manner are either partially or completely

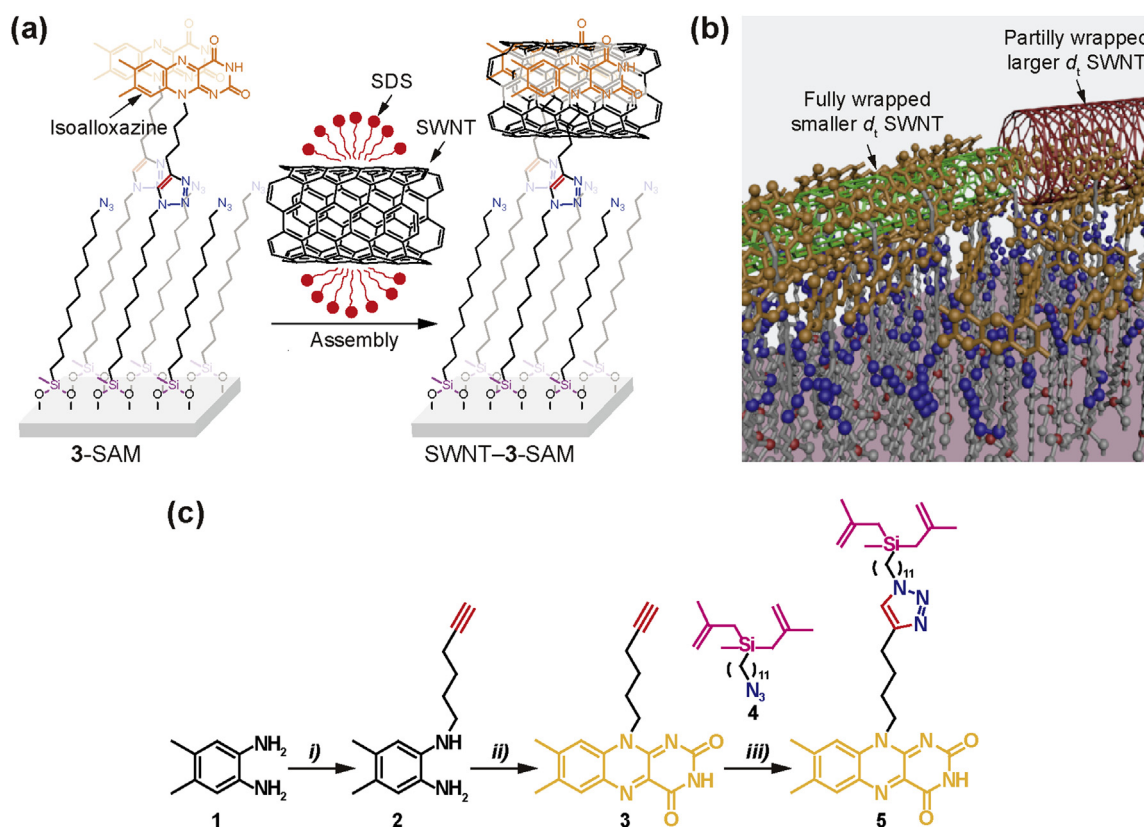


Fig. 1. (a) Flavin-terminated self-assembled monolayer (3-SAM) for the direct assembly of SWNT from a SDS dispersion. (b) Pictorial illustration of diameter-selective SWNT wrapped by flavin tethered to 3-SAM. Orange, blue, gray, and red colors denote isoalloxazine, azide, alkyl chain, and silicon group respectively. (c) Synthetic scheme for isoalloxazine (orange) containing dimethylsilylamine (magenta).^{*}

^{*} Conditions: i) 6-chloro-1-hexyne/TEA, 125 °C, 12 h, 15%; ii) alloxan, CH_3COOH , B_2O_3 , 60 °C, 3 h, 40%; iii) 4, CuSO_4 , sodium ascorbate, 1:1 THF/H₂O, r.t., 2 h, 64%. (A colour version of this figure can be viewed online.)

buried through wrapping in a d_t specific manner by isalloxazine rings in the functionalized SAM. Specifically, the flavin-SAM, having a spacer length of *ca.* 3 nm, preferentially captures SWNTs with smaller $d_t < 1$ nm while repelling ones with larger d_t values. Furthermore, resonance Raman spectroscopy (RRS) was utilized to confirm preferential *met*-SWNTs assembly with d_t below 1 nm. Finally, that preferential assemblies of SWNTs on the flavin-SAMs were demonstrated as compared to conventional hydrophobic surface by using a photolithography method. Buried, yet networked SWNT film resulted in electrical conductivity.

2. Results and discussion

2.1. Design and synthesis of Flavin-SAM precursors

The flavin-SAMs, **3**- and **5**-SAMs, explored in this study (Fig. 1a), are comprised of polymethylene-tethered isalloxazine moieties (orange) covalently linked through siloxy-ether groups (magenta) to the surface of a silica substrate. The dimethylsilyl group [40,41] rather than more common trichloro- or trimethoxy-silane functionalities was used for covalent attachment of the chain containing an isalloxazine ring to the silica substrate because the former does not undergo self-polymerization and it is stable in the presence of moisture [40,41]. These advantages enable isolation and quantification of the precursors used for surface functionalization [36,37].

The key synthetic intermediates **3** and **5** used for preparation of the flavin-SAMs were prepared through the route shown in Fig. 1c. The isalloxazine containing acetylene terminal **3** was produced a two step route beginning with reaction of 4,5-dimethyl-1,2-phenylenediamine (**1**) [35,42,43] with 6-chloro-1-hexyne to give **2** which was then reacted with alloxan monohydrate to form isalloxazine **3** [44]. 10-(4-(1-(11-(Methylbis(2-methylallyl)silyl)undecyl)-1*H*-1,2,3-triazol-4-yl)butyl) isalloxazine (**5**) was prepared by CuSO₄ promoted Click reaction of acetylene **3** with (11-Azidoundecyl)(methyl)bis(2-methylallyl)silane (**4**), using procedures described in the literature [45–47]. The structures and purities of **3** and **5** were assigned by using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy (Fig. S1 and Fig. S2), elemental analysis (EA), and FT-IR spectroscopy (Fig. S3).

In one route for formation of the flavin-SAMs, the dimethylsilyl-linked azide **4** was reacted with a piranha-cleaned quartz substrate in presence of trifluoromethanesulfonic acid [45–47] to generate the intermediate **4**-SAM containing a siloxy-ether linked, azide terminated polymethylene chain. Then, **3**-SAM was produced by Click reaction of **4**-SAM with the isalloxazine ring containing acetylene **3** in presence of CuSO₄. In another route, **5**-SAM was synthesized through surface modification of silica by using dimethylsilyl-linked isalloxazine **5**, which was generated by copper catalyzed Click reaction between acetylene **3** and azide **4**. Thus, the difference between **3**- and **5**-SAMs is the presence in the former of remaining (unreacted) immobilized azide groups on the substrate surface. It is important to note that in its fully extended form, the tether length is *ca.* 3 nm, which is adequate for positioning of the flavin moiety for interaction with the outmost surface of SWNT considering both 1 nm average d_t of the high pressure carbon monoxide (HiPco) process SWNT [6] and the van der Waals (vdW) distance between SWNT and flavin (*i.e.*, 0.34 nm) [34].

2.2. Characterization of Flavin-SAMs

FT-IR spectroscopy was used to characterize the functional groups present in **4**- and **3**-SAMs [48,49]. Because attempts to obtain FT-IR spectra on these SAMs on a flat substrate using

attenuated reflection accessories were unsuccessful, the analogously modified mesoporous silica (MPS) based **4**- and **3**-SAMs which have the larger surface area (30 m²/g) needed to facilitate measurements were prepared. Inspection of Fig. 2a shows that the FT-IR spectrum of MPS only (black) contains several broad bands at 1991, 1878 and 1635 cm⁻¹ which originate from overtones and combinations of Si–O stretching [50], respectively. In addition, bands at near 2900 cm⁻¹ seems to be associated with alkyl adsorbates. The FT-IR spectrum of **4**-MPS (red) contains four prominent bands in the 3100–1500 cm⁻¹ region, including one corresponding to asymmetric stretching of the azide at 2100 cm⁻¹ (green shaded area) [48,51], which confirms the success in covalent grafting with **4**. In addition, bands at 2925 and 2856 cm⁻¹ that correspond to methylene asymmetric and symmetric stretches are prominent in the spectrum of **4**-MPS [52]. Their absorption frequencies suggest that alkyl moieties in this substance are loosely packed as compared to those (*i.e.*, 2930 and 2850 cm⁻¹) in highly crystalline polyethylene [53]. The FT-IR spectrum of **3**-MPS, formed by Click reaction of **3** with **4**-MPS, contains a weak band at 1738 assigned to strong C=O stretch of the isalloxazine unit [42,54], bands at 1578 and 1545 cm⁻¹ attributed to amide II and amide IV (out-of-plane) stretching of uracil group in isalloxazine (orange shaded area) [55] and a lower intensity azide band at 2099 cm⁻¹. Those bands are in good agreement with those of **5** (green trace). FT-IR results indicate that not all azide reacted with **3**.

Quantitative analysis of functionalization degree was obtained from EA owing to self-polymerization tolerant nature of dimethylsilyl [40,41]. The results of EA show that **4**-MPS contains respective C, H and N contents of 1.62, 0.62, and 0.74% which corresponds to the presence of 0.174 mmol/g of azide groups on the surface of this substrate, which is in accordance with earlier findings [40,41]. A calculation based on the surface area of MPS [see Supporting Information (SI)] indicates that the density of azide groups on silica is *ca.* 3.5×10^{14} molecules/cm² (Table 1).

UV–vis absorption band intensities along with the known extinction coefficient (ϵ) of the isalloxazine chromophore permit calculation of the surface densities of flavin moieties in **3**- and **5**-SAMs. The absorption spectra of samples following after each functionalization step are displayed in Fig. 2b. The spectrum of **4**-SAM (dashed line) vs. quartz as a blank contains featureless absorption tail along with a maximum at 266 nm (ϵ of 300 L/mol·cm) [56,57] associated with azide groups. The material formed following Click-coupling of acetylene **3** to **4**-SAM (*i.e.*, as-prepared **3**-SAM, red) exhibits absorption maxima at 222, 270, 354 and 448 nm that resemble absorption bands (*i.e.*, 222, 273, 335, and 442 nm) of **3** in methanol (MeOH) (5×10^{-7} M, green). The maxima at 354 and 448 nm originate from respective type I and II π - π^* electronic transitions of the isalloxazine moiety whose directions are depicted in the inset in Fig. 2b [58–60]. Considering that spectra were recorded on similar concentrations, the slight shift differences between the maxima of **3** in MeOH and **3**-SAM likely originates from solvatochromic effects on isalloxazine ring [61–63]. Because flavins are known to form self-aggregates [60,64] and physisorbed flavin derivatives are released during SWNT assembly process, **3**-SAM was further washed with 1 wt% SDS in water to give SDS-treated **3**-SAM (blue) that has 60% reduced in absorption intensities of the isalloxazine related bands. The degree of isalloxazine ring surface functionalization in SDS-treated **3**-SAM was calculated by using the absorbance at 453 nm along with the flavin extinction coefficient (see SI) of $10,406 \pm 24$ L/mol·cm obtained by linear regression analysis of absorption intensities of **3** at 442 nm at MeOH concentrations in the range of 0.5–50 μ M (Fig. S4). This value is similar to the one previously reported in the literature [37]. The functionalized isalloxazine density is found to be *ca.* 1.1×10^{14} molecules/cm², which is *ca.* 60%

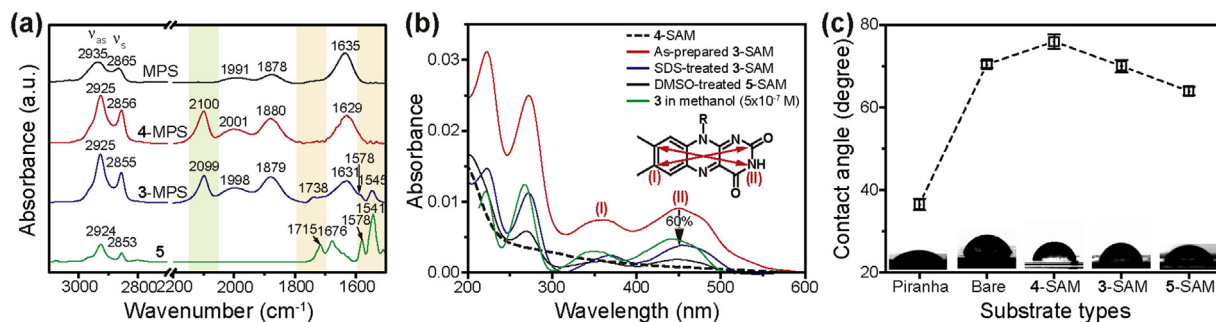


Fig. 2. Surface characterizations of functionalized SiO₂/Si substrates. (a) FT-IR spectra of as-received MPS (black), 4-MPS (red) and 3-MPS (blue) as compared to 5 (green). Green and orange shades indicate increasing and decreasing bands as proceeded surface reaction. (b) UV–vis absorption spectra of 4-SAM (dotted), as-prepared 3-SAM (red), SDS-treated 3-SAM (blue), and 5-SAM (black) on a quartz substrate in comparison with 3 in methanol (5×10^{-7} M, green). Inset illustrates the transition dipoles I and II of the isoalloxazine moiety corresponding to 354 and 448 nm absorptions, respectively. (c) Contact angle variations according to surface treatment and functionalization. Error bars indicate standard deviation. (A colour version of this figure can be viewed online.)

of that (1.85×10^{14} molecules/cm²) of closely packed trapezoidal structured isoalloxazines (54 Å²) assembled on highly oriented pyrolytic graphite [65]. The overall surface densities of azide groups in each functionalized SAM are given in Table 1. The results show that ca. 31% of the azide groups in 4-SAM undergo Click reaction with 3 in case of SDS-treated 3-SAM, which agrees with the result derived by using the FT-IR measurements. Similarly, 5-SAM following removal of physisorbed 5 by treatment with either dimethyl sulfoxide (DMSO) or SDS solutions has nearly half the flavin surface density as compared to that of SDS-treated 3-SAM, which might explain the slight difference between the contact angles of 5- and 3-SAMs (see below). This result also suggests that a sufficiently high free volume exists around the flavin groups in the functionalized SAMs (Fig. 1a).

Contact angle measurements on 3-, 4- and 5-SAMs further led to hydrophobicity displayed in the data and images of Fig. 2c. The results show that quartz has an average contact angle of $70.4 \pm 0.9^\circ$ and piranha-treated quartz has a lower contact angle of $36.5 \pm 1.3^\circ$, indicating that both possess hydrophilic surfaces. In contrast, terminal azide-containing 4-SAM has an average θ of $75.9 \pm 1.3^\circ$ that is in good agreement with the literature [48,66,67] while 3- and 5-SAMs have respective contact angles of $70.0 \pm 1.5^\circ$ and $63.9 \pm 1.0^\circ$.

2.3. Characterization of SWNT assembled on 3- and 5-SAM

Having successfully prepared and fully characterized 3- and 5-SAMs, we next assessed whether they are capable of promoting assembly of SWNTs in SDS dispersions. For this evaluation, a widely-used SDS-SWNT dispersion was prepared by using a sonochemical method using HiPco tubes [6,68]. The dispersion resulting from aqueous suspension of the HiPco SWNT in 1 wt% SDS was subjected to ultracentrifugation step to remove SWNT bundles and carbonaceous impurities (see Methods) [6,7]. The UV–vis–near IR (NIR) spectrum of the resulting SDS-HiPco dispersion (blue trace of Fig. 3a) contains well-defined first (e_{11}^S , 950–1350 nm) and second (e_{22}^S , 600–950 nm) semiconducting excitonic transitions along with first metallic transitions (e_{11}^M , 440–645 nm) corresponding to

HiPco tubes individualized by SDS [5,6,30,69,70]. 3- and 5-SAMs were separately immersed SDS-HiPco suspensions overnight, and iteratively washed with 1 wt% SDS solution/deionized (DI) water in order to eliminate physisorbed SWNTs. Although having nearly 100 times much less intense absorbances than those of SDS dispersions, SWNTs assembled on 3- and 5-SAM display excitonic transitions. Importantly, e_{11}^S and e_{22}^S of the immobilized HiPco on 3-SAM (i.e., HiPco–3-SAM, green trace) have peak positions that are intermediary between those of SDS-HiPco (blue) and FMN-HiPco (red) dispersions (Fig. S5). This result suggests that not fully wrapped π - π interactions occur between SWNTs and isoalloxazines in SWNT immobilized by 3-SAM. Judged by absorption, a lesser degree of SWNT assembly takes place using 5-SAM (black), probably because it has lower surface flavin density.

Because the observed absorption shifts mentioned above might originate from bundling of SWNTs [71], PL activities of SWNTs on the SAMs stemming from band gap of individual SWNTs according to their (*n*, *m*) chiralities were probed [23,25]. PL excitation (PLE) maps of solid phase HiPco–3-SAM along with the aqueous samples of dispersed SWNTs by FMN and SDS were measured by using a series of emission spectra obtained at various excitation wavelengths to obtain precise e_{11}^S and e_{22}^S [7,34]. Despite arising from weak absorbance (ca. 10^{-5} level), the PLE map of HiPco–3-SAM (Fig. 3b) displays profound PL activities originating from various (*n*, *m*) SWNT species (diamond) and it differs from that of 3-SAM (Fig. S6). Interestingly, although various surface charges site on silica surfaces typically quench PL of SWNTs [72], the flavin tether in 3-SAM creates a secure environment in which these sites are not able to interact with the SWNTs. To the best of our knowledge, this is the first example in which SWNT immobilized by a SAM display PL activity. Similar to the absorption spectroscopy results, the PL emission wavelengths e_{11}^S and e_{22}^S of HiPco–3-SAM (e_{11}^S and e_{22}^S from various chiralities are given in Table S1) are positioned in between those of aqueous FMN-HiPco (square) and SDS-HiPco (triangle) dispersions (Fig. 3c and d, respectively) [12,34,73]. It is known that π - π interactions associated with flavin wrapping promote a redshift of SWNT PL as compared to that caused by anionic

Table 1
Surface functionalization density and reaction degrees of functional SAMs as compared to 4-SAM.

Substrate type	Surface density ($\times 10^{14}$ cm ⁻²)	Density ratio of flavin/azide (%)	Determination method
4-SAM	3.5	N/A	EA
As-prepared 3-SAM	2.6	74	Absorbance
SDS-treated 3-SAM	1.1	31	Absorbance
DMSO-treated 5-SAM	0.53	15	Absorbance
Isoalloxazine on HOPG	1.85	54	STM [65]

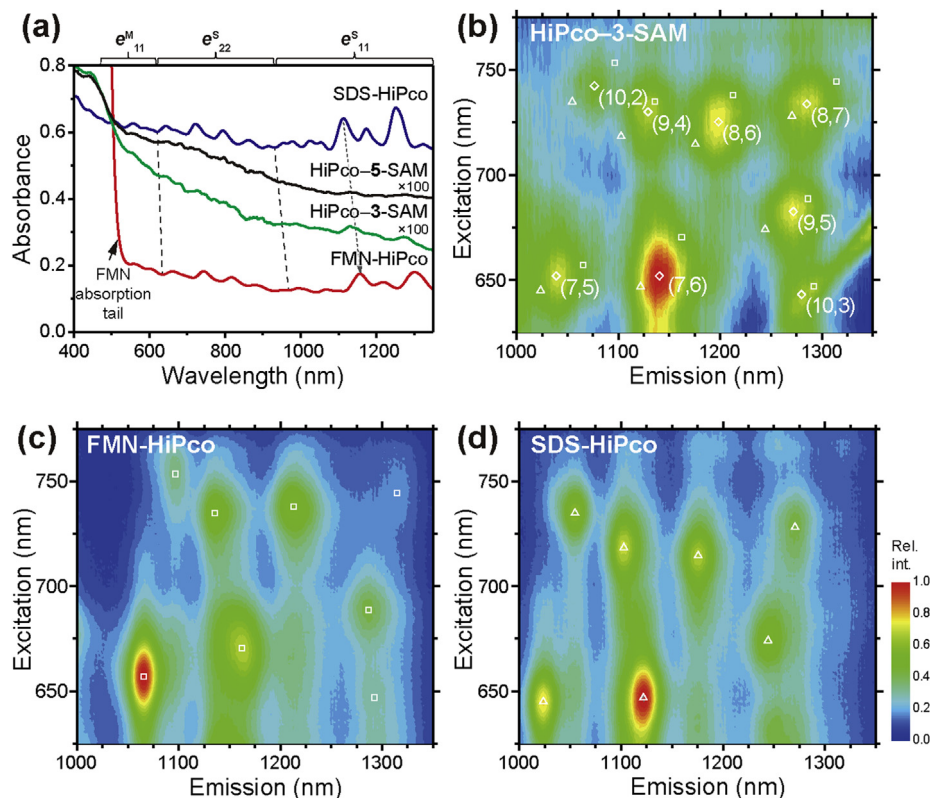


Fig. 3. (a) UV–vis–NIR absorption spectra of HiPco–3-SAM (green) and HiPco–5-SAM (black) as compared to those of SDS-HiPco (blue) and FMN-HiPco (red) dispersions. Dashed and dotted lines indicate borderlines between the optical transitions of SWNTs and bathochromic shift of e_{11}^s , respectively. The spectra of SDS-HiPco, HiPco–5-SAM, HiPco–3-SAM were multiplied and followed by offset by 0.4, 0.4 and 0.25, respectively, for visual clarity. PLE maps of (b) solid-state HiPco–3-SAM on a quartz, (c) FMN-HiPco, and (d) SDS-HiPco aqueous dispersions. Diamond, square, and triangle symbols indicate e_{11}^s and e_{22}^s positions of (n, m) SWNTs derived from HiPco–3-SAM, FMN-HiPco, and SDS-HiPco dispersions, respectively. (A colour version of this figure can be viewed online.)

surfactants [34,38,39]. The existence of intermediate PL wavelengths indicates that the flavins around the SWNTs are presumably imperfect because of heterogeneous interface during the assembly. Also, HiPco–3-SAM displays similar PL abundance with SDS-HiPco dispersion, suggesting that SDS-HiPco adsorption is important step for the assembly. In addition, HiPco immobilized on 5-SAM (Fig. S7) displays less-intense PL activity as compared to that of HiPco–3-SAM presumably owing to lower degree of grafted flavin functionality, in agreed with absorption measurement. The remainder of this study focused on characterization of HiPco–3-SAM.

The imperfect wrapping of HiPco by isoalloxazine rings is further evidenced by heterogeneous peak broadening of HiPco–3-SAM which occurs to a greater extent than in spectra of FMN- and SDS-SWNT. For instance, full widths at half maximum of (7,5) tube (i.e., 37.4 meV) on 3-SAM (Fig. S8) are larger than those of FMN- and SDS-wrapped (7,5) (30.0 and 28.3 meV, respectively). This result suggests that heterogeneity originating from the SWNT environment such as imperfect flavin wrapping plays a role in peak broadening [35].

AFM provided information about the morphology of HiPco–3-SAM. The large area image (Fig. 4a) shows that SWNTs are assembled in a random network structure on 3-SAM (see more image in Fig. S9) with a density of *ca.* 38 tubes/ μm^2 and an average length of *ca.* 226 nm (Fig. S10). This assembly is extended to SWNT with longer length which is often limitation for SWNT sorting methods including density ultracentrifugation [29] and sephacryl-based chromatography [30]. The use of SWNT with longer length prepared by brief 30 min sonication during the preparation of SDS-

HiPco prompts similar assembly as well (see Figs. S11a–d for AFM height image, length histogram, absorption spectra, and Raman spectra). AFM height and its histogram (Figs. S11a and 11b) shows SWNT assembled on 3-SAM and its median length is *ca.* 467 nm. Upon dipping into the longer HiPco dispersion, the absorption spectrum (Fig. S11c) revealed that 3-SAM promotes assembly of longer HiPco with slightly higher extent as compared to that from the shorter HiPco. Raman spectrum which will be discussed in later discussion (Fig. S11d) showed that 3-SAM has less selectivity towards smaller- d_t HiPco sample. Nevertheless, the closer investigation of individual SWNTs in HiPco–3-SAM (panel (i) to (iv) in Fig. 4b) shows average heights varying from 0.3 to 0.67 nm, that are much smaller than that of FMN-HiPco (1.36 nm, Fig. 4c), generated by deposition of a FMN-HiPco dispersion on a SiO_2 substrate. The results of height analysis and a consideration of the median d_t of HiPco (i.e., 1 nm) and its vdW distance (i.e., 0.34 nm) from FMN [34], indicates the existence of partially buried SWNTs in HiPco–3-SAM. Moreover, the height pitch of a SWNT on 3-SAM in the few tens of nm range originates from the flavin assembly [34,39,74]. The phase images given in Fig. S12a and Fig. S12b show that a vivid pattern of flavin assemblies exist on the SWNTs which lessen with increasing d_t .

The fully and partially buried sidewalls of the SWNTs in HiPco–3-SAM infers that the SWNT surface is non-uniform as a consequence of lack of full organization of the flavins (Fig. 4d and e). Considering 3 nm length of 3-SAM, the SWNT in 3-SAM exists in a buried configuration owing to a helical assembly of congregated flavin groups surround it. To determine if SWNT selection is based on its d_t , SWNTs with larger d_t values were assembled on the 3-SAM

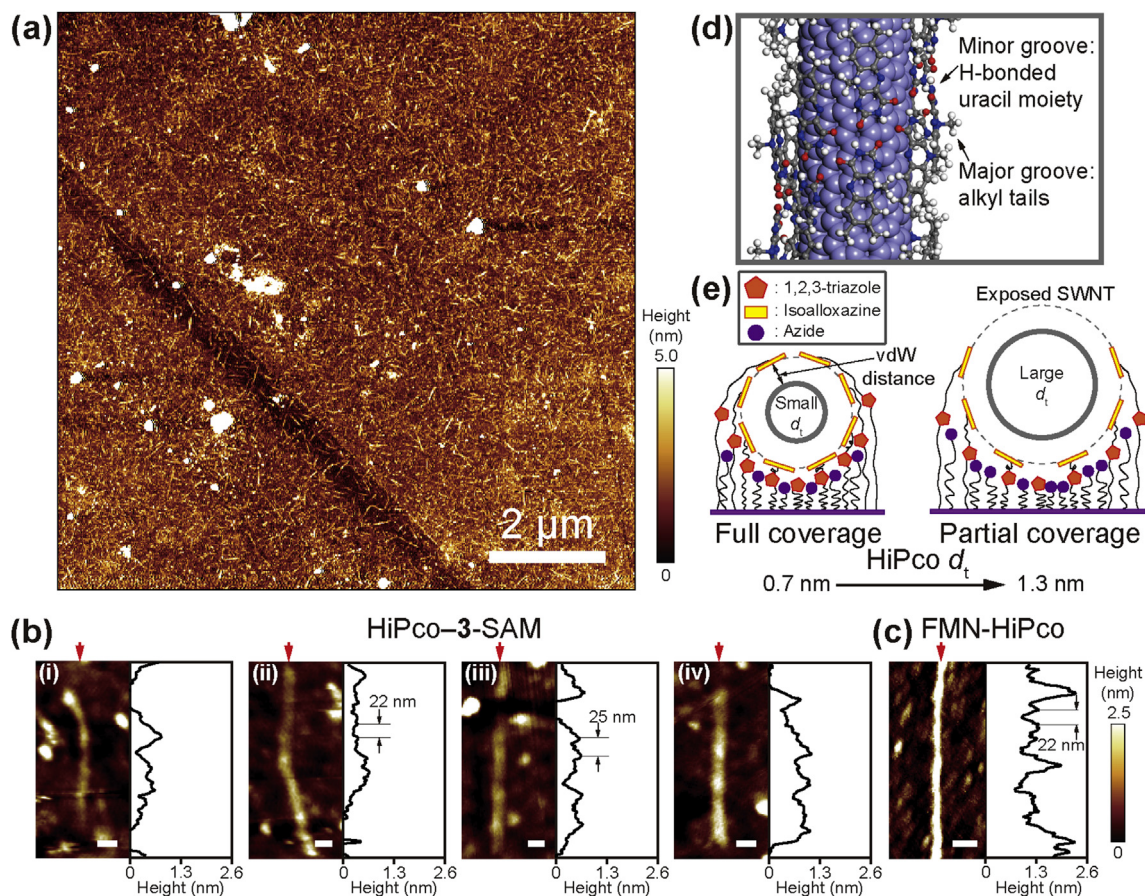


Fig. 4. Morphology analysis of the assembled HiPco-3-SAM by using AFM. (a) Large-area topographic image of HiPco-3-SAM. (b) Panel (i) to (iv): zoom-in height images of individualized SWNTs and height profiles along a line indicated by a red arrow, with increasing d_t from HiPco-3-SAM. (c) Height image of FMN-HiPco deposited on a SiO₂/Si substrate. Scale bars of (b) and (c): 25 nm. (d) Schematics of the flavin helix on a SWNT. Lumiflavin or *N*-methyl isoalloxazine instead of compound **3** was displayed for visual clarity. (e) Schematics of d_t -selective flavin assembly of 3-SAM on SWNT. (A colour version of this figure can be viewed online.)

surface. Plasma-torch grown SWNT (PSWNT) which has a larger average d_t of 1.3 nm was dispersed by using SDS in a manner similar to that used for assembly from a HiPco dispersion. In Fig. S13a are displayed absorption spectra of PSWNT suspended in SDS which show that optical transitions (e_{22}^S , e_{33}^S , and e_{11}^M) occur at longer wavelengths as compared to those for HiPco owing to the confinement effect on the larger PSWNT. Corresponding PLE maps (Fig. S13b and Fig. S13c, respectively) demonstrate that SDS-PSWNT displays PL arising from several chiralities assigned to (13,2), (10,5), and (9,7) while PSWNT on 3-SAM does not have any PL activity [75]. Along with AFM measurement (Fig. S13d) and Raman analysis (Figs. S13e–f), this result clearly indicates that the length of the flavin linking chains in 3-SAM is pivotal for d_t -governed selective assembly of SWNTs.

EFM provides clear evidence of the buried SWNTs in HiPco-3-SAM [76,77]. As illustrated in Fig. 5a (see Methods), EFM is a tool employed to image electric fields and potentials in SWNT circuits [78,79] and ferroelectricity [80], enabling detection of SWNTs embedded in a polymer matrix [81]. EFM operates by conducting an initial scan for height topography using tapping mode of AFM, followed by carrying out a lift-mode scan with applied bias between a conductive tip and the sample [76,77]. Therefore, the SWNT network embedded in 3-SAM is expected to display electrical conductance and a phase lag owing to tip-SWNT interaction. To carry out EFM, individualized SWNT 3-SAM rather than networked structure via a diluted SDS-HiPco dispersion was in order to achieve better visualization. In Fig. 5b and c are displayed a AFM

height and corresponding EFM phase images, respectively. Inspection of the AFM images shows the presence of SWNTs indicated by green arrows, and the corresponding EFM phase reveals even invisible tubes (red arrows) in the height image. This observation clearly indicates that completely buried SWNT exists beneath 3-SAM layer as is shown pictorially in Fig. 1b.

2.4. Assembly kinetics of HiPco-3-SAM with different dipping conditions

Kinetics of the SWNT assembly and optimum assembly conditions were investigated by varying dipping conditions (*i.e.*, with/without sonication and vertical/horizontal dipping) which affect assembly kinetics. Our previous study [12] showed that the electrical performance of thin film transistor is highly dependent on dipping manner. Moreover, it will become clear in later discussion that to increase adsorption rate requires increased SWNT concentration and applied sonication promotes effective incensement of SWNT concentration by increased collision. In addition, the mild sonication produced by a 70-W bath sonicator rather than a 300-W probe sonicator has been utilized for the assembly to minimize SWNT shortening. The repetitive dipping/measurement processes stopped when substrate absorbances reach to a plateau. As shown in Fig. 6a, a SDS-wrapped SWNT in aqueous dispersion is reversibly adsorbed on 3-SAM with respective adsorption and desorption constants defined by k_a and k_d . The rate of SWNT assembly was determined by measuring the intensities of bands in the absorption

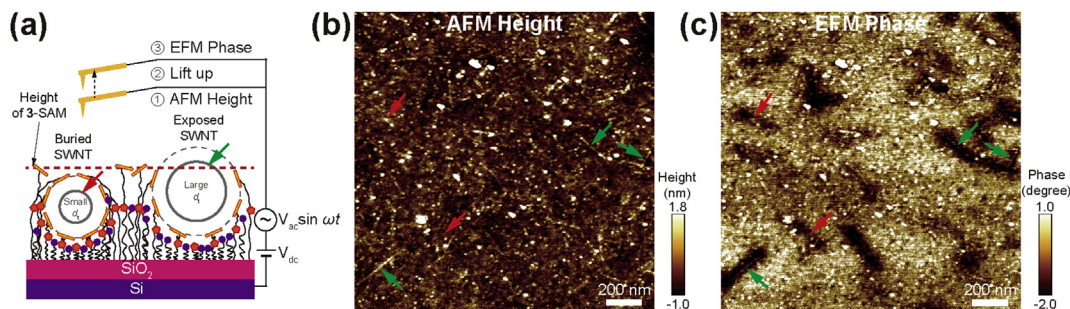


Fig. 5. Buried SWNT in 3-SAM by EFM analysis. (a) Schematics of EFM measurement procedure for completely and partially buried SWNTs as indicated by red and green arrows, respectively. V_{ac} and V_{dc} denote alternative and direct voltages, respectively. (b) AFM height image, and (c) corresponding EFM phase image of HiPco–3-SAM. Note that height maximum is 1.8 nm in (b). (A colour version of this figure can be viewed online.)

spectrum of a sample of 3-SAM after each of several dippings into a SDS-HiPco dispersion. Initially, horizontal dipping without sonication leads to a slow increase in the assembly of HiPco on the SAM surface kinetics over a dipping time up to 600 min (Fig. S14a). In contrast, SWNT assembly takes place more rapidly when horizontal dipping is accompanied with mild bath sonication (Fig. 6b). Upon horizontal and vertical dippings with sonication, the exciton peaks of the HiPco tubes increase with time and reach maxima at dipping time of ca. 150 min, while horizontal dipping only displays much slower adsorption kinetics. The surface coverage θ of SDS-HiPco assembled on 3-SAM was evaluated by using a Langmuir isotherm and the assumption that SWNTs are assembled as a monolayer by employing Eqn (1) [82]:

$$\frac{d\theta}{dt} = k_a(1 - \theta)c - k_d\theta \quad (1)$$

where θ is the fraction of the surface covered, $(1 - \theta)$ is the fraction of surface exposed, and c is the SWNT concentration. Integration of

Eqn (1) yields the time course for monolayer formation as shown in Eqn (2),

$$\theta(t) = \frac{c}{c + (k_d/k_a)} (1 - \exp[-(k_a c + k_d)t]) \quad (2)$$

which can be simplified by the substitution $k_{obs} = k_a c + k_d$ and $K' = c/(c + (k_d/k_a))$ to give Eqn 3

$$\theta(t) = K' [1 - \exp(-k_{obs}t)] \quad (3)$$

where k_{obs} and K' are the observed rate and coefficient for exponential saturation, respectively. The absorption background was subtracted in order to obtain kinetic profiles. In Fig. 6c are given the background-subtracted evolutions of the intensities of the peak at 1272 nm that is originating from *sem*-SWNT for horizontal dipping with sonication (black) and without sonication (red), and vertical dipping with sonication (blue). The SWNT concentration was determined to be $0.8 \mu\text{g mL}^{-1}$ using the absorption intensity of the

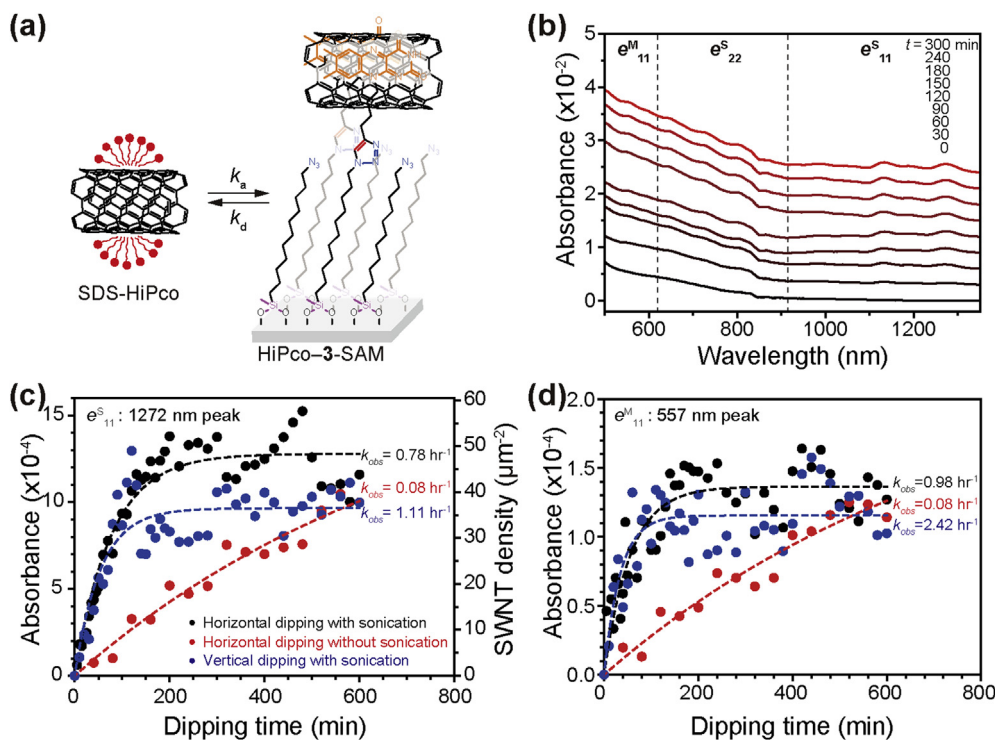


Fig. 6. Kinetics of assembly formation from a SDS-HiPco dispersion in 3-SAM according to the dipping time t and methods. (a) Schematics of adsorption and desorption of SDS-HiPco in 3-SAM. (b) Absorption spectrum evolution of HiPco–3-SAM with dipping time t and mild bath sonication in a horizontal substrate dipping. The spectra were offset by 0.003 for visual clarity. Kinetics of absorption and fitting results of (c) 1272 nm, and (d) 557 nm peaks from horizontal dipping with (black), without (red) sonications, and vertical dipping with sonication (blue), representing *sem*- and *met*-SWNT, respectively. (A colour version of this figure can be viewed online.)

π plasmon band located at *ca.* 273 nm [83]. In Table S2 is summarized the peak-dependent kinetic behavior corresponding to optical transitions for SWNT electronic types corresponding to various metallic and semiconducting peaks over the vis-NIR range, including 557 and 597 nm, 650 and 732 nm, and 1133 and 1272 nm for e_{11}^M , e_{22}^S and e_{11}^S , respectively [30,84]. Fitting the data for changes in the 1272 nm band to Eqn (3) gives a k_{obs} for horizontal dipping with sonication of 0.78 hr^{-1} , which is about ten times faster than that (0.08 hr^{-1}) for dipping without sonication and corresponds to a nominal value of *ca.* 50 SWNTs/ μm^2 . Because same concentrations of the dispersion are used for the assembly, the $k_{obs} = k_{ac} + k_d$ value suggests that collision between SDS-SWNT and 3-SAM is facilitated by sonication. In the case of vertical assembly, k_{obs} is 1.1 hr^{-1} . Moreover, the desorption rate k_d values are *ca.* 537, 780, and 1030 times larger than those of k_{ac} for horizontal dipping without sonication, with sonication and vertical dipping with sonication, respectively. This result underscores the observation that assembly is dependent on the dipping methods. Especially, horizontal assembly seems to be subject to gravitational force, promoting more SWNT assembly. In addition, considering Eqns (2) and (3), SWNT assembly is consequence of the concentration of SWNT and that concentrations over mg mL^{-1} are suitable for assembly. Moreover, k_{obs} of *met*-SWNT (*i.e.*, 597 and 557 nm peaks for e_{11}^M) is much larger than those of *sem*-SWNT (732 and 650 nm for e_{22}^S and 1272 and 1133 nm for e_{11}^S , respectively). This result suggests that, as compared to the *sem*-counterpart, *met*-SWNT is preferentially adsorbed on 3-SAM, which stands in contrast with the high-purity *sem*-SWNT enrichment promoted by using a flavin dispersion [12]. Those inconsistency indicates that although they share a similar chemical entity, the result of surface and solution assembly differ significantly in terms of *sem*-vs. *met*-selectivity.

RRS is a powerful tool used to obtain information (relative abundances) about the *met*- and *sem*-chiralities of SWNTs. In this RRS analysis, the radial breathing mode (RBM) bands of SWNTs were measured which is inversely proportional to d_t [70,85]. Laser with 532 and 632.8 nm as excitation sources was utilized to probe HiPco in the d_t range from 0.7 to 1.3 nm, to probe mostly *met*-SWNTs and *met*/*sem*-SWNT ratios for each excitation, respectively (see Kataura plot in Fig. S16 for details) [70,85]. In Fig. 7a is displayed the normalized RBM region with respect to *met*-(9,3) chirality arising from excitation at 532 nm. Peak was deconvoluted by Lorentzian shape. While large- d_t *met*-SWNTs (*>ca.* 1 nm) [*i.e.*, (13,1), (9,6), and (10,4) species] are clearly observed in FMN- and SDS-HiPco dispersions, the proportion of these types of nanotubes become reduced by more than half following three SAM dippings. This result suggests that smaller- d_t *met*-SWNT below 1 nm are mainly absorbed by 3-SAM. Moreover, assembly conditions such as dipping direction and sonication (see middle panels in Fig. 7a and b) does not affect the relative abundances of electronic types much. In order to verify selectivity according to electronic types of SWNT, in Fig. 7b are displayed normalized RBM regions arising from excitation at 632.8 nm, which contain larger- d_t *met*- and smaller- d_t *sem*-SWNTs. As indicated by the dotted line, the $150\text{--}230 \text{ cm}^{-1}$ region contains broad bands originating from several *met*-chiralities with larger d_t [*i.e.*, (12,6), (9,9), and (13,4)] whereas the $230\text{--}310 \text{ cm}^{-1}$ region contains several bands associated with *sem*-SWNTs with smaller d_t [*i.e.*, (10,3), (11,1), (7,6), (7,5), and (8,3)]. A comparison shows that HiPco assembled on 3-SAM exhibits weaker *sem*-bands as compared to those from FMN-HiPco and SDS-HiPco samples, an observation that is in accord with preferential adsorption of *met*-SWNT in the assembly process.

2.5. Site-specific assembly of HiPco–3-SAM and resulting resistance

To determine if the functionalized SAM is superior for

assembling SWNT vs. hydrophobic substrate, site-specific assembly of HiPco on 3-SAM and octadecyltrichlorosilane (OTS) treated substrates was evaluated. For this purpose, patterned substrates were prepared using conventional photolithography (see Methods). Line patterns were generated by using 2/50 nm thick Ti/Au thermal evaporation, as shown in Fig. S17. The remaining areas were functionalized by using OTS to produce OTS-SAM regions. Then, the Au and Ti layers were then stripped away by treating the substrate with KI/I_2 solution followed by trifluoromethanesulfonic acid solution, respectively. The newly exposed SiO_2 areas were sequentially functionalized with 4 and 3 to produce 3-SAM regions, followed by washing with 1 wt% SDS solution/water. In Fig. 8a is shown the optical microscope (OM) image of the HiPco treated patterned substrate. The corresponding AFM phase image near the interface, shown in the insets in Fig. 8b, contains clearly observed contrasts between the SWNT densities. These results demonstrate that assembly of SWNTs occurs preferentially on 3-SAM as compared to other commonly used hydrophobic surface.

Successful d_t -selective and site-specific immobilization of SWNT network prompts us to measure resistance of the prepared HiPco network on 3-SAM. For accurate measurement, we have utilized four probe resistance measurement which has been prepared by evaporating Au electrodes *via* thermal evaporation using a polyimide mask placed on HiPco–3-SAM (see Methods). Especially, inner Au electrodes for measuring voltage drop were separated by 2 mm to check long range resistance. Fig. 8c shows a photograph of the device. The average resistance was $505 \pm 11 \text{ k}\Omega$ and, assuming 1 nm film thickness of SWNT networks, conductivity is 2000 S/m . This result demonstrates the successful incorporation of conductive SWNT network by simple dipping into widely-available SDS-SWNT dispersion albeit few nm thickness.

We have devised coral reef-like flavin-derived functional SAMs to immobilize SWNT network in d_t -selective manner for a given substrate. The innate sorting capability of this method does not necessitate additional sorting method which is often required for advanced optoelectronic applications. It might be also useful as a stationary phase of column chromatography if 3-SAM is assembled on silica gel to selectively capture SWNT with d_t -selective fashion from as-dispersed SWNT by commonly used SDS. In addition, it is cost-effective since this method only needs exact small amount of SWNT to cover a given substrate by simple dipping method in as-dispersed SWNT solution, and reuses the mother dispersion unless SWNT population according to electronic types does not alter significantly owing to the repetitive adsorption. Since commercially-available sorted SWNT is one of the most expensive components (*e.g.* 199\$ for 1 mg *met*-SWNT, Nanointegris), this method using as-dispersed SWNT and 3-SAM will find a way as an alternative for SWNT sorting method. In addition, in conjunction with SAM technology which has been instrumental for photolithography process to change surface properties, the demonstrated preferential assembly of SWNT over hydrophobic substrate will be useful for the fabrication of SWNT-based optoelectronic devices.

3. Conclusion

In the investigation described above, a method was developed for diameter-specific noncovalent functionalization of SWNTs, which employs novel flavin-terminated self-assembled monolayer. The precursor for the functionalized SAM was fabricated using Click reaction of *N*-hexynyl flavin and a polymethylene-linked azide containing a terminal dimethylsilyl group. The flavin containing moieties can be covalently attached to various SiO_2 surfaces including silicon substrate, quartz, and mesoporous beads. The flavin functionalized SAMs can be employed to assemble SWNTs readily from a SDS-SWNT dispersion. The flavin terminal groups

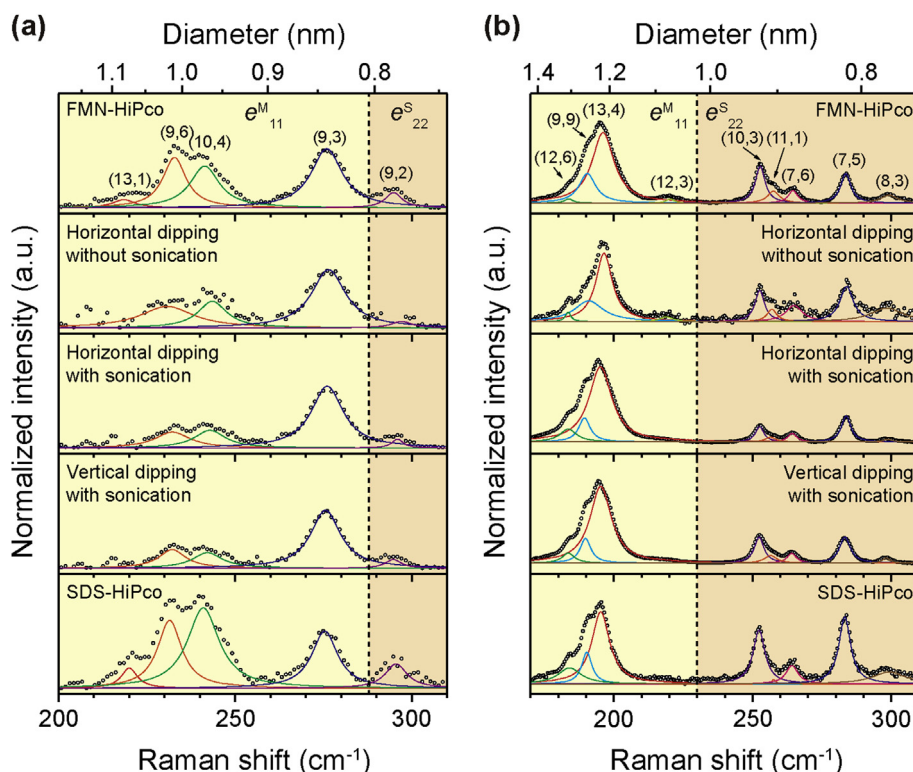


Fig. 7. RBM analysis of SWNT species assembled in **3**-SAM by using various dipping methods as compared to drop-cast samples from SDS- and FMN-HiPco dispersions, probed by using (a) 532 nm, and (b) 632.8 nm lasers. Chirality assignment and abundance was obtained by lorentzian deconvolution. (A colour version of this figure can be viewed online.)

linked *via* aliphatic spacers to the solid support enable SWNTs to bind strongly to be photoluminescent and electrically conductive assembly. Moreover, **3**-SAM is capable of promoting preferential assembly of SWNTs having diameters below 1 nm. The results of AFM and EFM studies clearly demonstrate that SWNTs in the assembled network are either fully or partially embedded in flavin wrappings. Moreover, absorption of SWNT networks on **3**-SAM follows a Langmuir isotherm with apparent rate constants that are in the hour regime. Especially, important is the observation that rate of assembly of *met*-SWNT on **3**-SAM is larger than for *sem*-SWNT. Furthermore, Raman analysis shows that smaller- d_t *met*-SWNTs below 1 nm are preferentially assembled on the SAM and smaller- d_t *sem*-SWNTs below 1 nm are not. Using this adsorption protocol, site-specific assembly of SWNTs can take place on **3**-SAM patterned substrates. The film-forming method is economical because it requires the use of only small amounts of SWNT dispersions as compared to thick network film from the transfer

method. Overall, this study has demonstrated that a rational strategy can be utilized to design a system for assembling individual SWNTs with diameter- and metallicity-specificity, and a controlled deposition rate. In conjunction with existing photolithography techniques, the use of **3**-SAM provides a novel approach to integrate individualized random SWNT networks into existing silicon-based technologies in future microelectronics and sensory applications.

4. Experimental

4.1. Materials and instrumentation

All chemicals were purchased from either Sigma-Aldrich or TCI. All solvents and chemicals were reagent grade and used as received. A silica gel with 240–400 mesh (Merck) was used for flash column chromatography. Precautions were taken to avoid

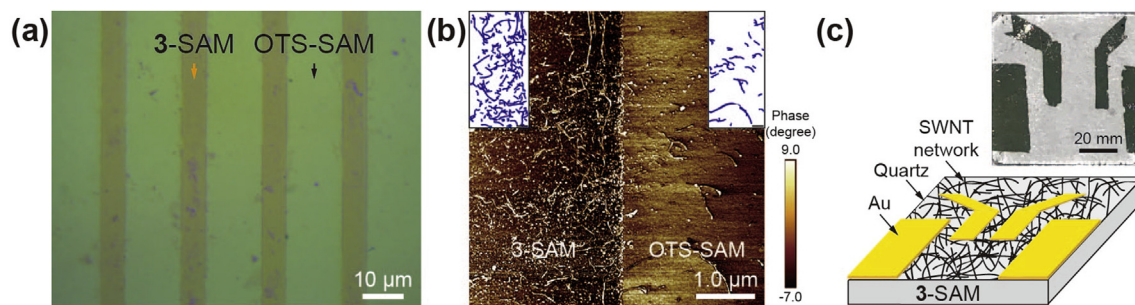


Fig. 8. Site-specific assembly of SWNT in **3**-SAM over hydrophobic SAM (i.e., OTS-SAM) patterned by using conventional photolithography. (a) OM image of alternative line patterns of **3**-SAM (brown) and OTS-SAM (green). (b) AFM phase image of interfacial region from **3**- and OTS-SAMs. Inset: pictorial illustration of SWNT abundance of (d). (c) Schematics of HiPco–**3**-SAM with Au electrodes for four probe measurement. Inset: a photograph of the device. (A colour version of this figure can be viewed online.)

prolonged exposure of the synthesized isalloxazine derivatives and functionalized substrate to direct sunlight. ^1H and ^{13}C NMR spectra were acquired by using a FT-NMR spectrometer (Avance III HD 400, Bruker Biospin) operating at Larmor frequencies at 400 and 100 MHz, respectively, unless otherwise mentioned. EA with a less than $\pm 0.2\%$ uncertainty was conducted using an elemental analyzer (2400 CHNS/O series II, PerkinElmer) in the CHN acquisition mode and calibrated against acetanilide as a reference. FT-IR spectra were obtained by using FT/IR-4700 (JASCO) with 1 cm^{-1} resolution and KBr pellets prepared by mixing bare and functionalized MPS (SMB1000-10, Fuji Silysia Chem. Ltd., quoted surface area: $30\text{ m}^2/\text{g}$) with dried KBr powder. A fused quartz substrate (Lot # 29-01502-01, iNexus, Inc.) was used for surface functionalization. UV–vis–NIR absorption spectra were obtained by using a V-770, JASCO spectrometer and either a quartz cuvette with a 10 mm beam path or a quartz substrate with custom-made substrate holder. Contact angles were measured by using a contact angle goniometer (Phoenix 10, Surface Electro Optics), and the values and standard deviations were obtained by averaging five times. Smaller and larger d_t SWNTs prepared by using HiPco [86] and PSWNT [12], respectively, were purchased from Carbon Nanotechnology Inc. (Batch #R1-831 and Batch #R26-036, respectively) whose median d_t with distributions are $1.0 \pm 0.35\text{ nm}$ and $1.35 \pm 0.35\text{ nm}$, respectively. OM images were obtained by using a bright field up-right microscope (BX50, Olympus) with a CMOS camera. OTS-SAM was prepared by reacting piranha-cleaned substrate with OTS (10 mM) in toluene (10 mL) at r.t. for 12 h according to the literature procedure [87]. The resulting substrate was washed with toluene several times, and dried by using a N_2 stream. Fig. 1b was generated by using 3Ds Max®.

4.2. Synthesis

Flavin derivatives [35,42] along with dimethylsilane derivatives [45–47] were synthesized using previous methods.

Synthesis of N-(Hex-5-ynyl)-4,5-dimethylbenzene-1,2-diamine (2): A mixture of 4,5-dimethyl-1,2-phenylenediamine (**1**) (2.04 g, 15 mmol) and 6-chloro-1-hexyne (0.585 g, 5 mmol) in triethylamine (TEA) (20 mL) was stirred at 125°C for 12 h under nitrogen. After cooling and addition of methylene chloride (MC) (100 mL), the organic phase was separated, washed with aqueous 10% Na_2CO_3 solution (40 mL). The aqueous layer was extracted twice with MC ($2 \times 100\text{ mL}$). The combined organic extracts were dried over anhydrous MgSO_4 and concentrated in vacuo giving crude **2** with a thin layer chromatography (TLC) retention factor (R_f) of 0.48 with 95:5 MC/MeOH. This substance was purified by using flash chromatography on a silica gel in 95:5 MC/MeOH to produce 0.162 g of reddish crystals (15% yield); m.p. 55°C ; ^1H NMR (400 MHz, CDCl_3 with tetramethylsilane (TMS), δ , see Fig. S1) 6.53 (s, 1H), 6.46 (s, 1H), 3.18 (br s, 3H, NH and NH_2), 3.11 (t, $J = 6.8\text{ Hz}$, 2H), 2.27 (s, $J = 2.5\text{ Hz}$, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 1.98 (t, $J = 2.6\text{ Hz}$, 1H), 1.79 (q, $J = 6.5\text{ Hz}$, 2H), 1.68 (q, $J = 7.0\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3 with TMS, δ , see Fig. S2) 135.7, 131.9, 128.1, 126.0, 118.3, (d, $J = 3.0\text{ Hz}$), 113.8, (d, $J = 3.0\text{ Hz}$) 84.2, 68.6, 44.0, 28.7, 26.1, 19.3, 18.8, 18.3; Anal. calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2$ (M.W. = 216.32): C 77.73, H 9.32, N 12.95; found: C 77.46, H 9.4, N 12.63.

Synthesis of 10-(Hex-5-ynyl)-isalloxazine (3): A mixture of compound **2** (0.216 g, 1 mmol), alloxan monohydrate (0.160 g, 1 mmol), boric oxide (0.21 g, 6 mmol) and glacial acetic acid (10 mL) was stirred at 60°C for 3 h. The resulting reaction was quenched with water (100 mL) and was vacuum-dried. The yellow residue was extracted with MC which was dried over anhydrous MgSO_4 . The TLC R_f of the target compound **3** was 0.15 with 1:10 tetrahydrofuran (THF)/MC. **3** was purified by flash chromatography on a silica gel in 1:10 THF/MC to produce yellow crystals (40% yield);

m.p. 280°C ; ^1H NMR (400 MHz, CDCl_3 with TMS, δ , see Fig. S1) 8.63 (s, 1H), 8.09 (s, 1H), 7.52 (s, 1H), 4.77 (br s, 2H), 2.59 (s, 3H), 2.48 (s, 3H), 2.38 (td, $J = 2.8\text{ Hz}$, 2H), 2.06 (q, $J = 7.6\text{ Hz}$, 2H), 2.04 (t, $J = 2.8\text{ Hz}$, 1H), 1.81 (q, $J = 7.4\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3 with TMS, δ , see Fig. S2) 159.6, 155.3, 150.1, 148.5, 137.2, 136.1, 135.0, 132.9, 131.0, 115.4, 83.4, 69.5, 44.7, 25.7, 25.2, 21.7, 19.6, 17.9; FT-IR (KBr, see Fig. S3) $\nu = 3254, 3153, 3098, 3024, 2989, 2951, 2922, 2864, 2806, 2112, 1715, 1655, 1624, 1578, 1539, 1504\text{ cm}^{-1}$; UV–vis (MeOH): $\lambda_{\text{max}}(\epsilon) = 442\text{ nm}$ ($10,406 \pm 24\text{ L/mol}\cdot\text{cm}$); Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2\cdot 0.5\text{H}_2\text{O}$ (M.W. = 331.37): C 65.24, H 5.78, N 16.91, O 12.07; found: C 65.33, H 5.75, N 16.93, O 11.99.

Synthesis of (11-Azidoundecyl)(methyl)bis(2-methylallyl)silane (4): To a stirred solution of (11-chloroundecyl)(methyl)bis(2-methylallyl)silane (3.28 g, 9.56 mmol), prepared by using the reported method [40], and DMF (15 mL) were added sodium azide (1.25 g, 19.1 mmol). Mixture was stirred at 80°C for 4 h, cooled to the r.t., diluted with H_2O and extracted with diethyl ether. The organic layers were dried over anhydrous MgSO_4 and concentrated in vacuo to give (11-Azidoundecyl)(methyl)bis(2-methylallyl)silane (colorless liquid, 98% yield); ^1H NMR (400 MHz, CDCl_3 , δ , see Fig. S1) 4.54 (d, $J = 44\text{ Hz}$, 4H), 3.24 (t, $J = 6.8\text{ Hz}$, 2H), 1.71 (s, 6H), 1.59 (m, 2H), 1.56 (s, 4H), 1.26 (m, 16H), 0.57 (m, $J = 7.8\text{ Hz}$, 2H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , δ , see Fig. S2) 143.8, 108.9, 51.7, 33.9, 29.7, 29.7, 29.7, 29.5, 29.4, 29.1, 27.0, 25.9, 25.6, 23.9, 14.2, –4.2; Anal. calcd for $\text{C}_{20}\text{H}_{39}\text{N}_3\text{Si}$ (M.W. = 349.63): C 68.71, H 11.24, N 12.02, Si 8.03; found: C 68.56, H 11.92, N 12.80.

Synthesis of 10-(4-(1-(11-(Methylbis(2-methylallyl)silyl)undecyl)-1H-1,2,3-triazol-4-yl)butyl) isalloxazine (5): A mixture of 10-(hex-5-ynyl)-isalloxazine (**3**) (90 mg, 0.31 mmol), (11-azidoundecyl)(methyl)bis(2-methylallyl)silane (90 mg, 0.26 mmol), CuSO_4 (10 mol %) and sodium ascorbate (20 mol %) in 1:1 THF/ H_2O (50 mL) was stirred at r.t. for 2 h and then concentrated in vacuo. The residue was dissolved in MC (100 mL) and the mixture was extracted with water. Concentration of the MC solution in vacuo gave a residue that was subjected to flash column chromatography to give **5** as a dark yellow solid (120 mg, 64%); m.p. 120°C ; ^1H NMR (400 MHz, CDCl_3 with TMS, δ , see Fig. S1) 8.64 (s, 1H), 8.05 (s, 1H), 7.60 (s, 1H), 7.53 (s, 1H), 4.75 (br s, 2H), 4.56 (d, $J = 44\text{ Hz}$, 4H), 4.33 (t, $J = 7.2\text{ Hz}$, 2H), 2.88 (br t, $J = 6.0\text{ Hz}$, 2H), 2.61 (s, 3H), 2.45 (s, 3H), 1.94 (br m, 6H), 1.71 (s, 6H), 1.57 (s, 4H), 1.30 (m, 8H), 1.23 (s, 8H), 0.56 (t, $J = 7.6\text{ Hz}$, 2H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 with TMS, δ , see Fig. S2) 159.6, 155.3, 150.0, 148.9, 143.6, 137.3, 135.9, 135.0, 132.7, 131.1, 121.4, 115.6, 108.6, 50.3, 45.0, 33.7, 30.4, 29.55, 29.53, 29.43, 29.3, 29.0, 26.6, 26.5, 25.7, 25.6, 25.4, 24.4, 23.7, 21.6, 19.6, 14.1, –4.4; FT-IR (KBr, see Fig. S3) $\nu = 3155, 3074, 2966, 2924, 2853, 2799, 1715, 1676, 1637, 1578, 1541, 1508\text{ cm}^{-1}$; Anal. calcd for $\text{C}_{38}\text{H}_{57}\text{N}_7\text{O}_2\text{Si}\cdot\text{H}_2\text{O}$ (M.W. = 690.00): C 66.15, H 8.62, N 14.21, O 6.96, Si 4.07; found: C 65.94, H 8.64, N 14.17.

4.3. Preparation of various SAMs

4-, 3-, and 5-SAMs were prepared in sequential manner. Initially, a piranha-cleaned quartz substrate was immersed in a 150 μmol solution of **4** and 15 μmol trifluoromethanesulfonic acid in acetonitrile (3 mL) at r.t. for 12 h. The substrate was washed with MC and acetone thoroughly, and unbound compound **4** was removed by treatment with 1 wt% SDS solution for 12 h, followed by DI water washing to give **4-SAM**. **3-SAM** was prepared by immersing **4-SAM** substrate a solution of **3** (28 μmol), sodium ascorbate (8 μmol) and CuSO_4 (4 μmol) in 1:1 THF/water (20 mL) at r.t. for 2 h. The substrate was washed with copious amounts of THF and DI water. The unbound compound **3** was removed by dipping the substrate into 1 wt% SDS solution for 12 h, followed by DI water washing to give **3-SAM**. Finally, **5-SAM** was prepared using the same procedure used to generate **4-SAM** except DMSO was employed as solvent. An

identical method was used for forming surface functionalized MPS, used for FT-IR and EA measurements.

4.4. FMN- and SDS-SWNT dispersions

To prepare the FMN-SWNT dispersion, a mixture of HiPco-SWNT (1 mg, 83 μmol in carbon equiv), FMN (16 mg, 35 μmol) in H_2O (4 mL) was probe-sonicated at 300 W for 2 h. The resulting dispersion was centrifuged at 20,000 gravitational acceleration force (g) for 2 h using a swing-bucket rotor (SW 41 Ti, Beckman Coulter), giving a clear dark upper 80% supernatant that was collected. The SDS-SWNT dispersion was similarly prepared by bath-sonicating (Branson 1510, 70 W) a mixture of HiPco-SWNT (1 mg, 83 μmol in carbon equiv), SDS (10 mg, 34.7 μmol) in H_2O (1 mL) for 1 h and probe-sonicated for 5 h at 300 W. For HiPco with longer length, sonication time is reduced to 30 min while other conditions are similar. The resulting mixture was centrifuged at 80,000 g for 10 h, giving an upper 80% supernatant that was collected and its pH was adjusted to 10 to produce a clear dark solution. PSWNT dispersions were prepared in a similar manner.

4.5. SWNT assembly on 3- or 5-SAMs

3- and 5-SAM substrates were immersed in SDS-HiPco dispersion (10 mL) at r.t. for 12 h unless otherwise noted. The resulting substrates were treated with 1 wt% SDS solution to remove a physisorbed SWNT. For studies of the kinetics of SWNT immobilization, the sample after gentle washing with DI water was subjected to absorption measurements.

4.6. PLE measurement

All samples were subjected to PLE measurements by using a Spex Nanolog 3–211 spectrofluorometer (Horiba, Jobin-Yvon) equipped with a liquid nitrogen-cooled, single-channel InGaAs detector. Solid samples were mounted on a mounting accessory with rotation angle of 20° with respect to incident light angle to reject Rayleigh light. Both excitation and emission light intensities were corrected against instrumental variations using sensitivity correction factors. Excitation and emission wavelengths for HiPco (PSWNT) are 550–800 (800–1000) nm and 900–1400 (1200–1600) nm with slit widths of 14 nm and 10 nm, respectively. Respective acquisition times for liquid and solid sample are 5 and 100 s.

4.7. AFM and EFM measurements

AFM topography and EFM phase were acquired by using NX10 (Park systems). For AFM measurement, Al-coated silicon cantilever with a spring constant 37 N m^{-1} and a resonance frequency of 300 kHz (ACTA, App Nano) was utilized. The quoted radius of curvature is *ca.* 6 nm. Typically, 1024×1024 pixel images were collected. For EFM measurements, Au-coated silicon cantilever with a spring constant 7.4 N m^{-1} and a resonance frequency f_0 at 160 kHz (PPP-NCSTAu, Nanosensors) was utilized. The quoted radius of curvature is *ca.* 50 nm. Typically, 512×512 pixel images were collected. A tip voltage V_t of 10 V is applied to the cantilever. Scanning used one pass in the tapping mode for each line to acquire the topography and then a second pass of the same line to fly above the sample with a constant tip–sample separation by 18 nm. While scanning the sample in the lift-mode pass, the force gradient sensed by the tip changes the effective spring constant of the cantilever, modulating f_0 . As the phase lag between the drive and the cantilever oscillation has an approximately linear frequency near f_0 , the f_0 modulation can be imaged to produce a gray scale

plot of phase angle as a function of tip position.

4.8. Patterned substrate preparation

Fabrication of patterned substrates was performed using conventional photolithography on a 285 nm thick SiO_2/Si substrate. Metal evaporation was performed to obtain 5 μm wide Ti/Au pattern (2/50 nm in thickness) in which Ti was used as the adhesion promoter between Au and SiO_2 substrate. Au etching was performed by using aqueous KI/I_2 with $\text{KI}:\text{I}_2:\text{H}_2\text{O}$ ratio of 4 g: 1 g: 40 mL which exhibits an etch rate with *ca.* 1 $\mu\text{m}/\text{min}$ at r.t. The Ti layer has been removed by trifluoromethanesulfonic acid treatment for 4 h instead of a widely used mixture of HF/HNO_3 to preserve SAM layer.

4.9. RRS measurement

Raman spectra and mapping images were acquired mainly using a LabRam Aramis (He–Ne laser (632.8 nm), Horiba, Jobin-Yvon) and home-made Raman spectrometer (532 nm) in a backscattering configuration [88,89]. A laser power of 7.0 mW/cm^2 , 50s exposure times and $50 \times$ objective lens (Olympus, LMPLFLN, N.A.: 0.5) were utilized to obtain RRS. Spectra from Stokes mode were collected with an internal reference to a Si peak at 520.84 cm^{-1} . d_t in nanometer and wavenumber were correlated using $\omega_{\text{RBM}} = 223 \text{ nm} \times \text{cm}^{-1}/d_t + 10 \text{ cm}^{-1}$ for *sem*-SWNT and $\omega_{\text{RBM}} = 218 \text{ nm} \times \text{cm}^{-1}/d_t + 17 \text{ cm}^{-1}$ for *met*-SWNTs, based on C–C distance of 0.142 nm, respectively [85]. Owing to large SiO_2 bands (*i.e.*, 152, 168, and 188 cm^{-1}) in the low frequency region, bare quartz and bare Si substrates were utilized to subtract RBM signals from SWNTs. Raman mapping was acquired by using 532 nm laser excitation and a raster-scanning method with a step-motor driven XY stage (Marzhauser Wetzlar GmbH & Co., 75 $\times$ 50 mm) with step size of 1 μm .

4.10. Four probe measurement

Metal electrode patterns for the electrical measurement were created on polyimide film (Lot # 963351, Nilaco Co.). Using a thermal metal evaporator (Kitano, Japan) equipped with a mechanical pump and turbo pump (up to 5.4×10^{-7} torr, Pfeiffer) in a series, Au electrodes were created on HiPco–3-SAM on quartz substrate via a thermal evaporation using the mask while the thickness was monitored by a quartz microbalance built inside. 30 nm thick Au electrodes were evaporated which is confirmed by AFM measurement, and the inner electrodes were separated by 20 nm. After initial calibration with a resistor with known resistance, the substrate was subjected to four probe measurement by using a program built in semiconductor characterization system (Keithley 4200-SCS), producing the average resistance value with the current at the level of 10^{-6} A.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Coral Reef-like Functionalized Self-Assembled Monolayers for Network Formation of Carbon Nanotube with Diameter Selectivity

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1. Calculation of azido functionalization density on a MPS

Since optical methods were not applicable for the determination of the azido densities on a MPS surfaces, EA was utilized. For this purpose, a MPS (SMB1000-10, Fuji Silysia Chem Ltd.) with a particle size is about 10 μm and surface area is 30 m^2/g in a quoted sheet was functionalized with compound **4**, and then subjected to obtain EA. The determined C, H, and N contents are 1.62, 0.62, and 0.74 atomic %, respectively. The loading rate of N with mol/g unit was calculated by the following equation: loading rate = (determined atomic % of N)/(atomic weight of N $\times$ number of N in azido functionality) in which number of N in azido functionality was applied to compensate azido molar density. The calculation shows that 0.176 mmol of azido moieties were loaded per gram of MPS. The loading rate was further divided by the quoted surface area of MPS, producing a surface density of $5.8 \times 10^{-10} \text{ mol}/\text{cm}^2$ (or $3.5 \times 10^{14} \text{ molecules}/\text{cm}^2$).

2. Calculation of flavin functionalization density for various SAMs

Because the absorbance of 3- and 5-SAM can be measured, flavin density per area for each SAM can be calculated by using the measured extinction coefficient with reference of closely-packed isoalloxazine foot print ($54 \text{ \AA}^2$) obtained by using scanning tunneling microscopy (STM) of flavin on highly oriented pyrolytic graphite (HOPG) surface according to the literature.¹ The Lambert's law $A = \varepsilon \cdot b \cdot c$ was used where A , ε , b , and c are absorbance, extinction coefficient, beam path length, and concentration, respectively. The calculated concentration c was $3.71 \times 10^{-10} \times b \text{ mol}/\text{cm}^2$ (i.e., $0.00386 = 10,406 \text{ L}/\text{mol} \cdot \text{cm} \times b \times c = 10,406 \times 10^3 \text{ cm}^2/\text{mol} \times b \times c$). The concentration is converted into moles per area by multiplying beam path b , leading to $3.71 \times 10^{-10} \text{ mol}/\text{cm}^2$. Furthermore, this value was divided by 2, considering the functionalization on both sides of the quartz surface. Then, surface density of isoalloxazine based on the measured absorbance is $1.12 \times 10^{14} \text{ molecules}/\text{cm}^2$ (or $1.85 \times 10^{-10} \text{ mol}/\text{cm}^2$).

On the other hand, since saturated flavin density which is inversion of foot print ($54 \text{ \AA}^2/\text{molecule}$) of isoalloxazine from STM study¹ is $1.85 \times 10^{14} \text{ molecules/cm}^2$, the surface coverage of as-prepared **3**-SAM is about 60.5% as compared to that of closed-packed flavin on surface. Similarly, flavin density of other SAM was calculated and was listed in **Table 1**.

Figure S1. ^1H NMR spectra of **2** - **5** in CDCl_3 with Larmor frequency at 400 MHz. Red, green, and blue asterisks were derived from CDCl_3 , methylene chloride, and water, respectively.

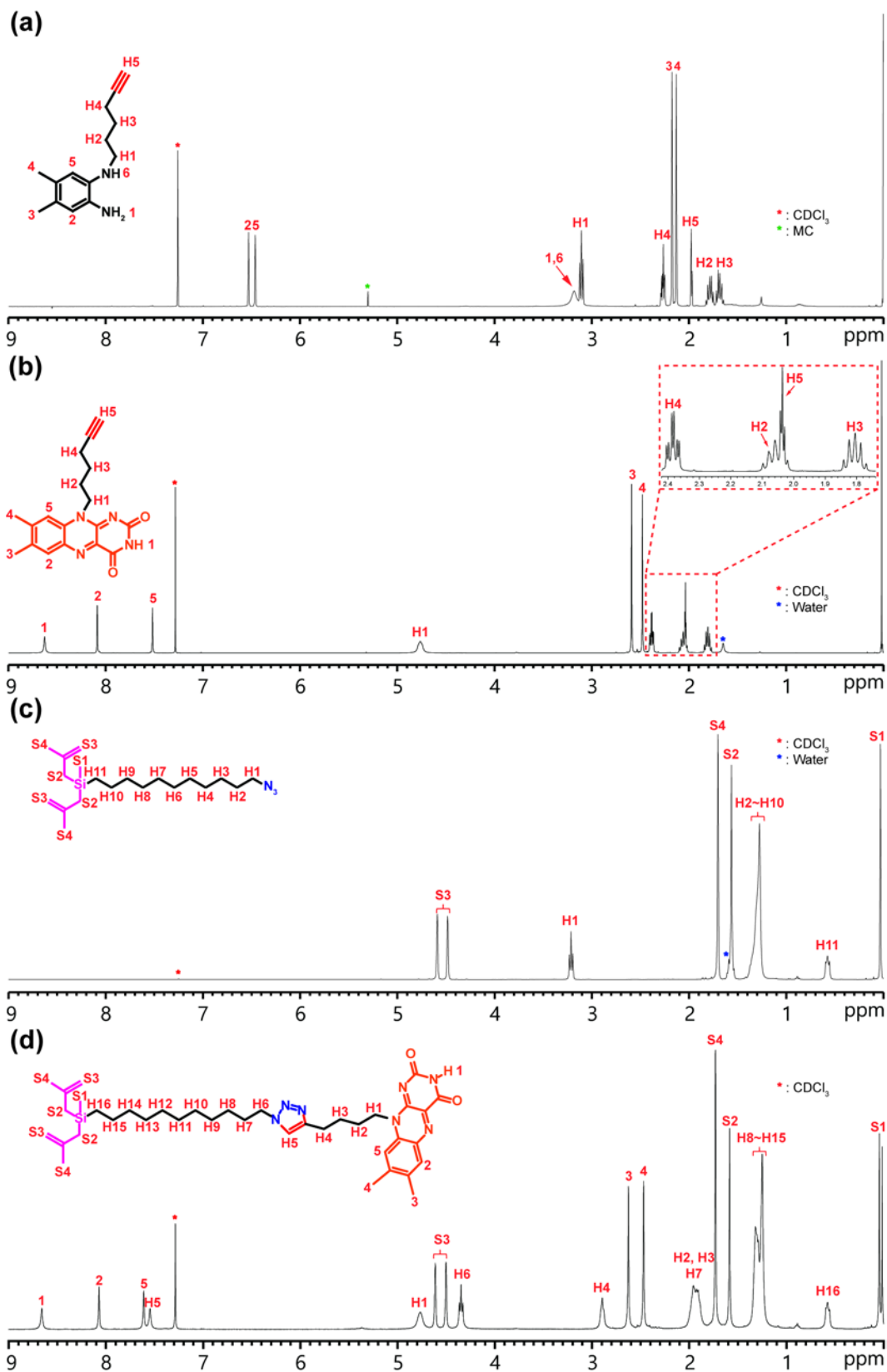


Figure S2. ^{13}C NMR spectra of **2** - **5** in CDCl_3 with Larmor frequency at 100 MHz. Asterisk were peaks from CDCl_3 .

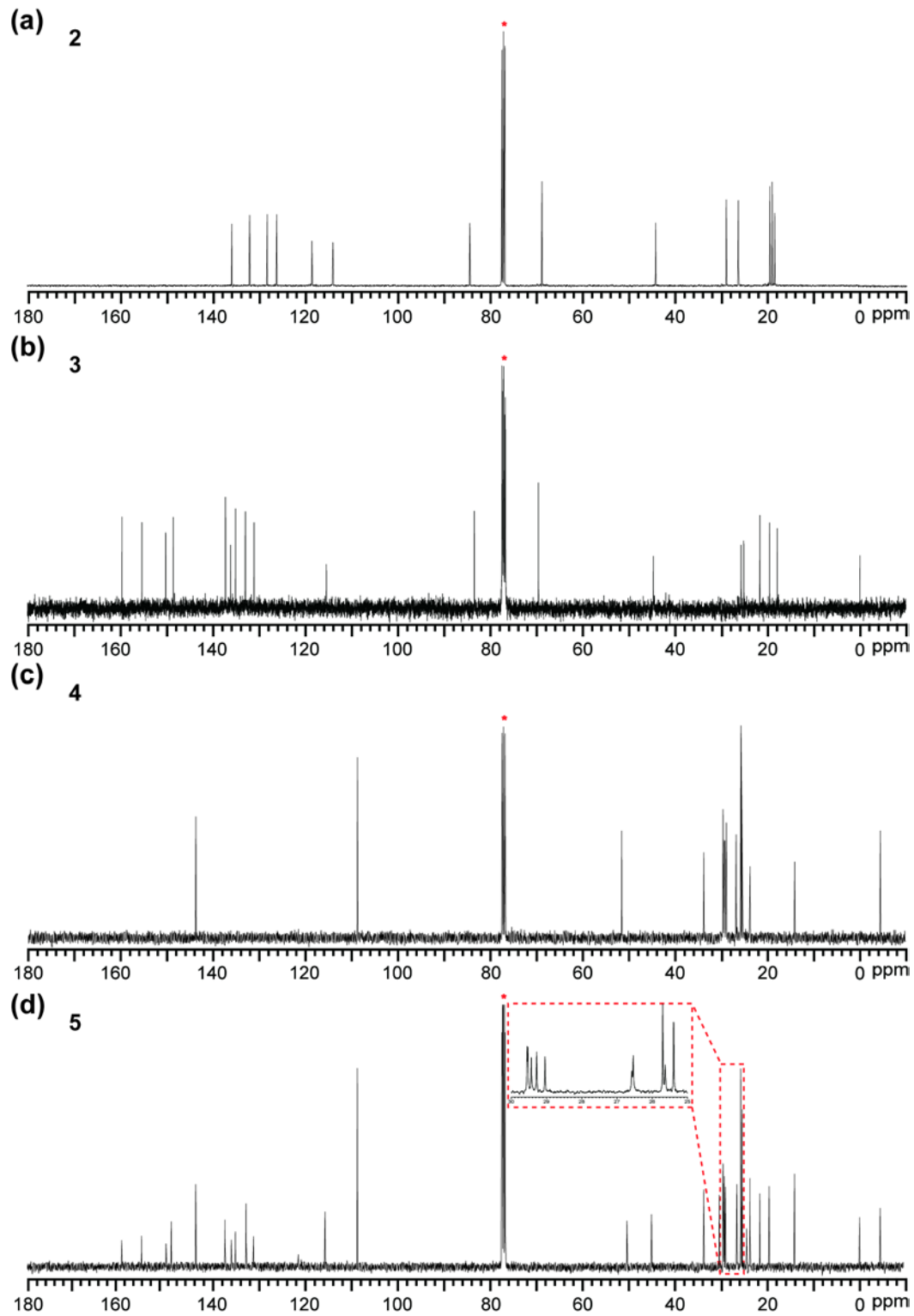


Figure S3. FT-IR spectra of **3** and **5**.

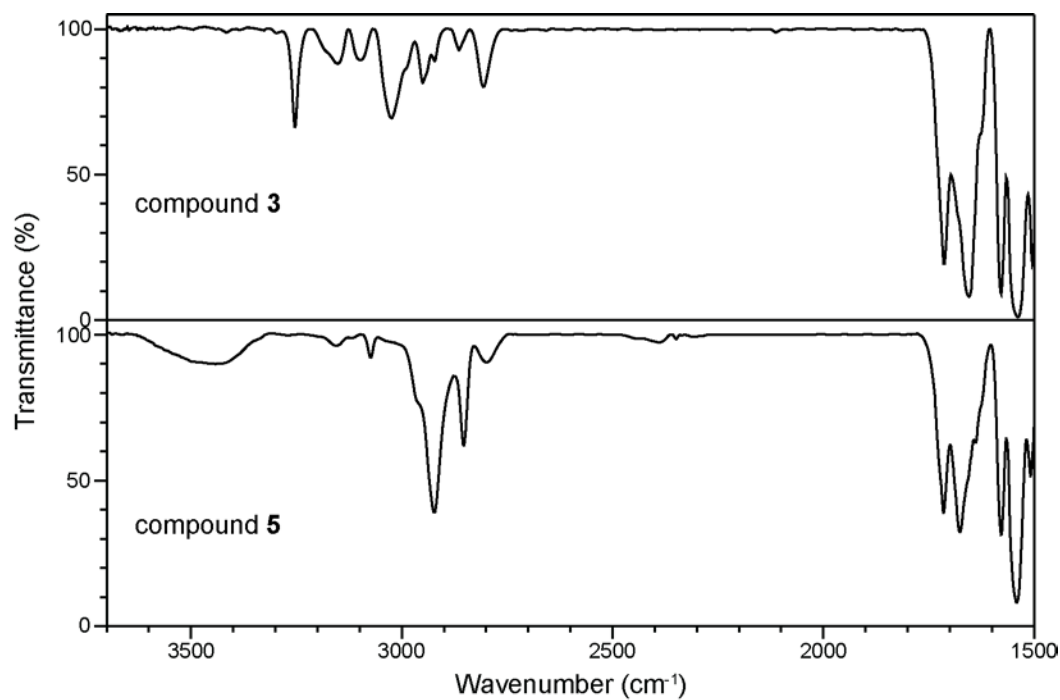


Figure S4. Extinction coefficient calculation of the band at 442 nm obtained from linear regression (dotted line) of compound **3** in methanol.

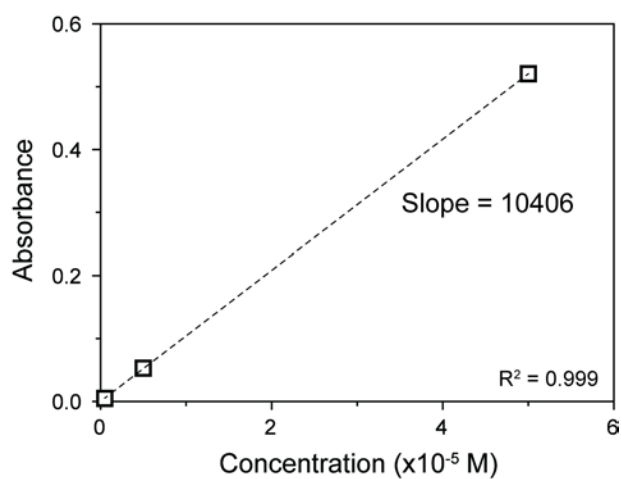


Figure S5. Background-subtracted UV-vis–NIR spectra of Figure 3a.

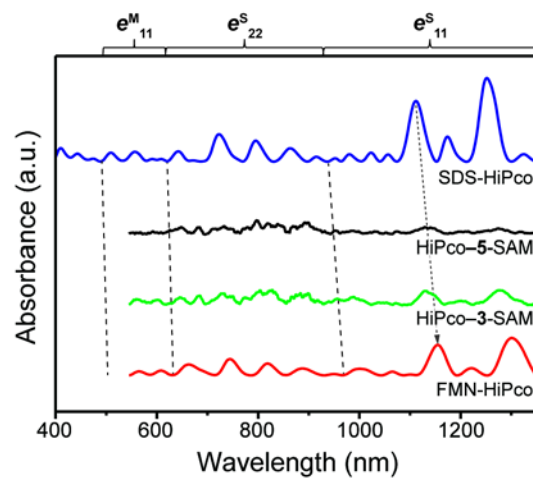


Figure S6. PLE map of 3-SAM alone.

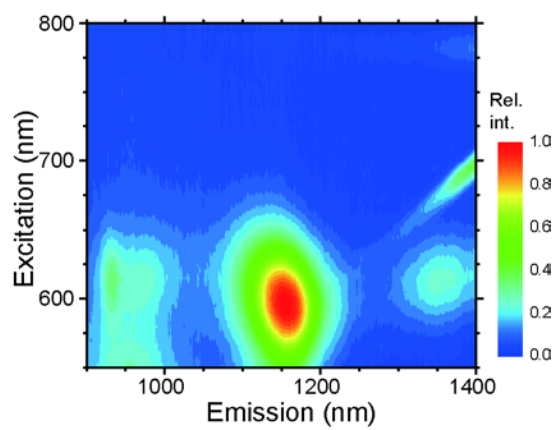


Figure S7. PLE map of HiPco-5-SAM.

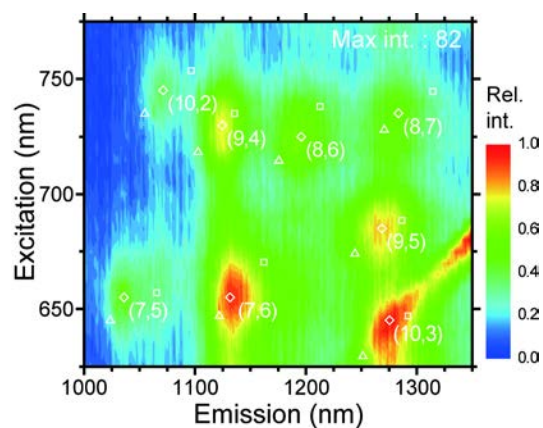


Figure S8. Comparison of FWHM of representative (7,5) tube in SDS dispersion (top), 3-SAM (middle), and FMN dispersion (bottom).

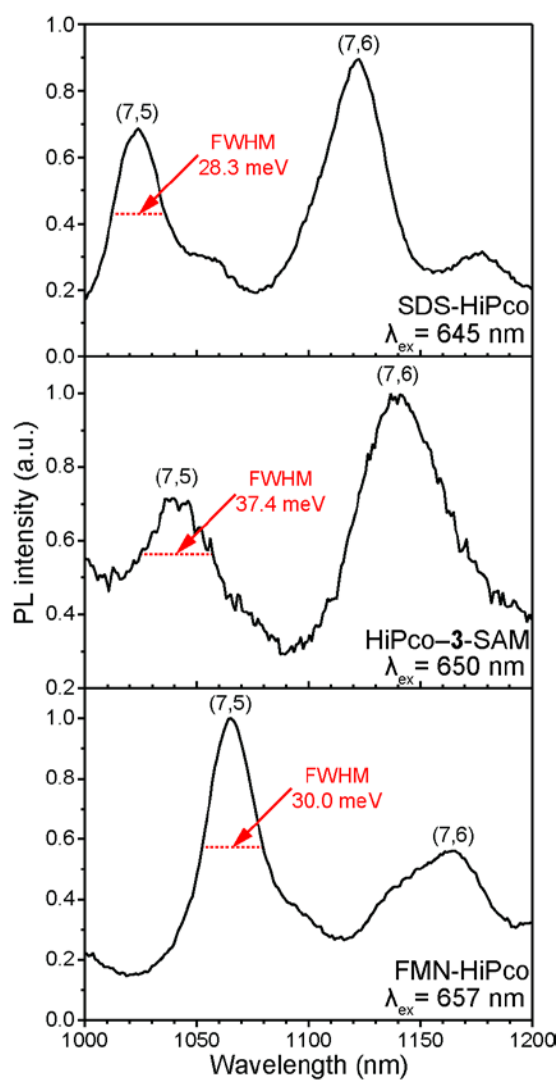


Figure S9. Additional AFM image of HiPco-3-SAM.

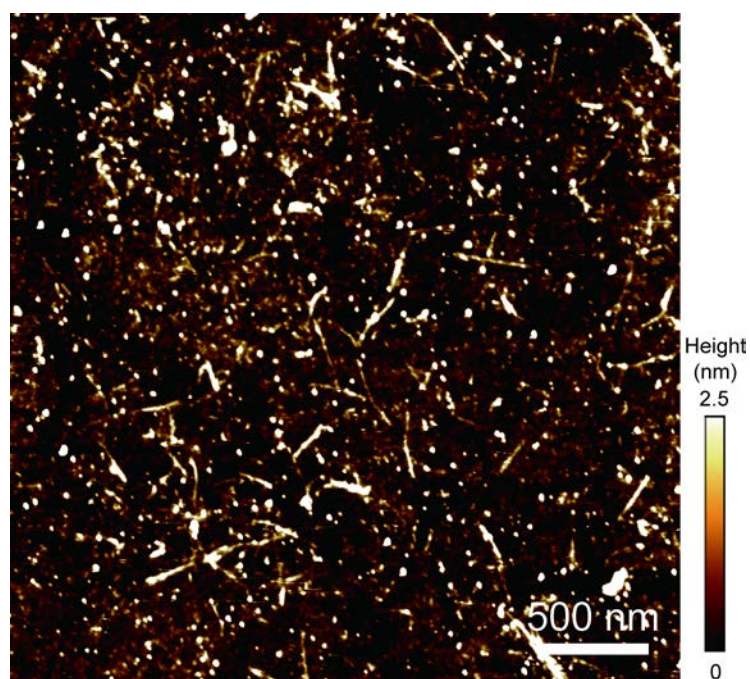


Figure S10. Length histograms of HiPco-3-SAM measured by using AFM.

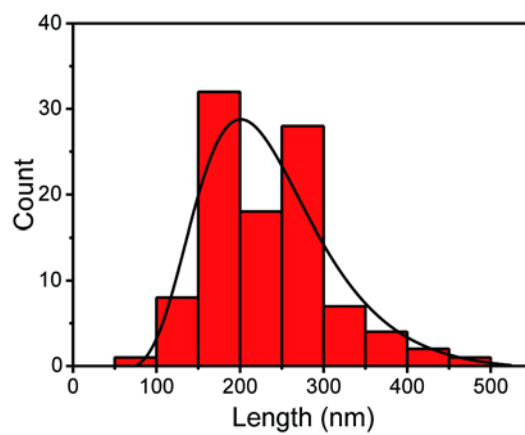


Figure S11. Characterization of assembly of longer HiPco assembled on 3-SAM. (a) AFM image of longer HiPco-3-SAM. (b) Length histograms of longer HiPco-3-SAM measured by using AFM. (c) UV-vis-NIR absorption spectra of longer HiPco-3-SAM (black) as compared to those of short HiPco-3-SAM (red). The spectra were offset for visual clarity. (d) RBM analysis of various length HiPco-3-SAM. Laser excitation: 532 nm.

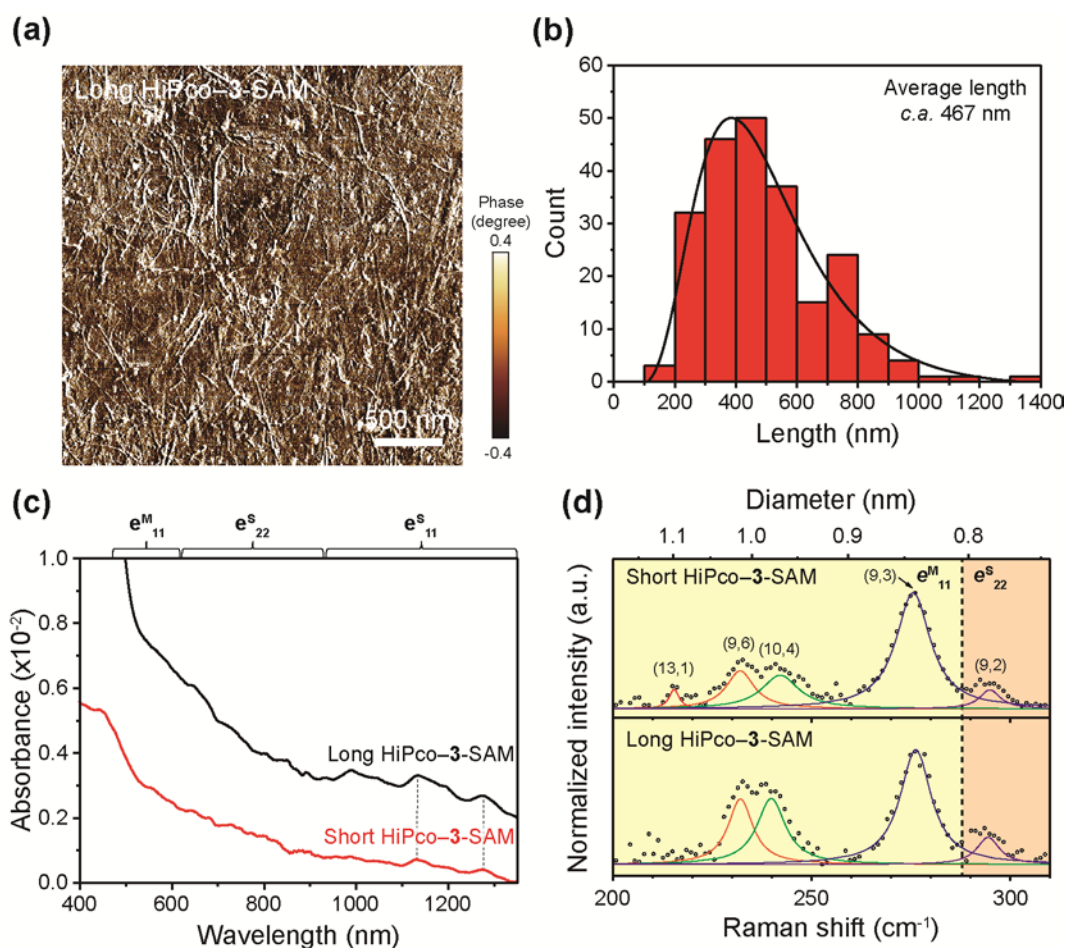


Figure S12. Corresponding AFM phase images. Scale bar: 25 nm.

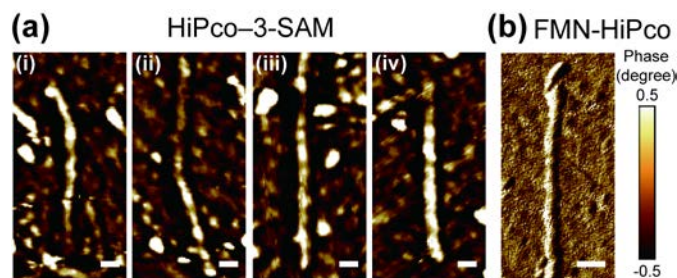


Figure S13. Characterization of large d_t SWNT assembled on 3-SAM. (a) UV-vis-NIR absorption spectra of PSWNT-3-SAM (black) as compared to those of SDS-PSWNT dispersion (blue). PLE map of (b) SDS-PSWNT dispersion, (c) $\times 10$ intensified PSWNT-3-SAM. (d) Large-area topographic image of PSWNT-3-SAM. (e-f) Raman analysis of PSWNT-3-SAM. Laser excitation: 532 nm.

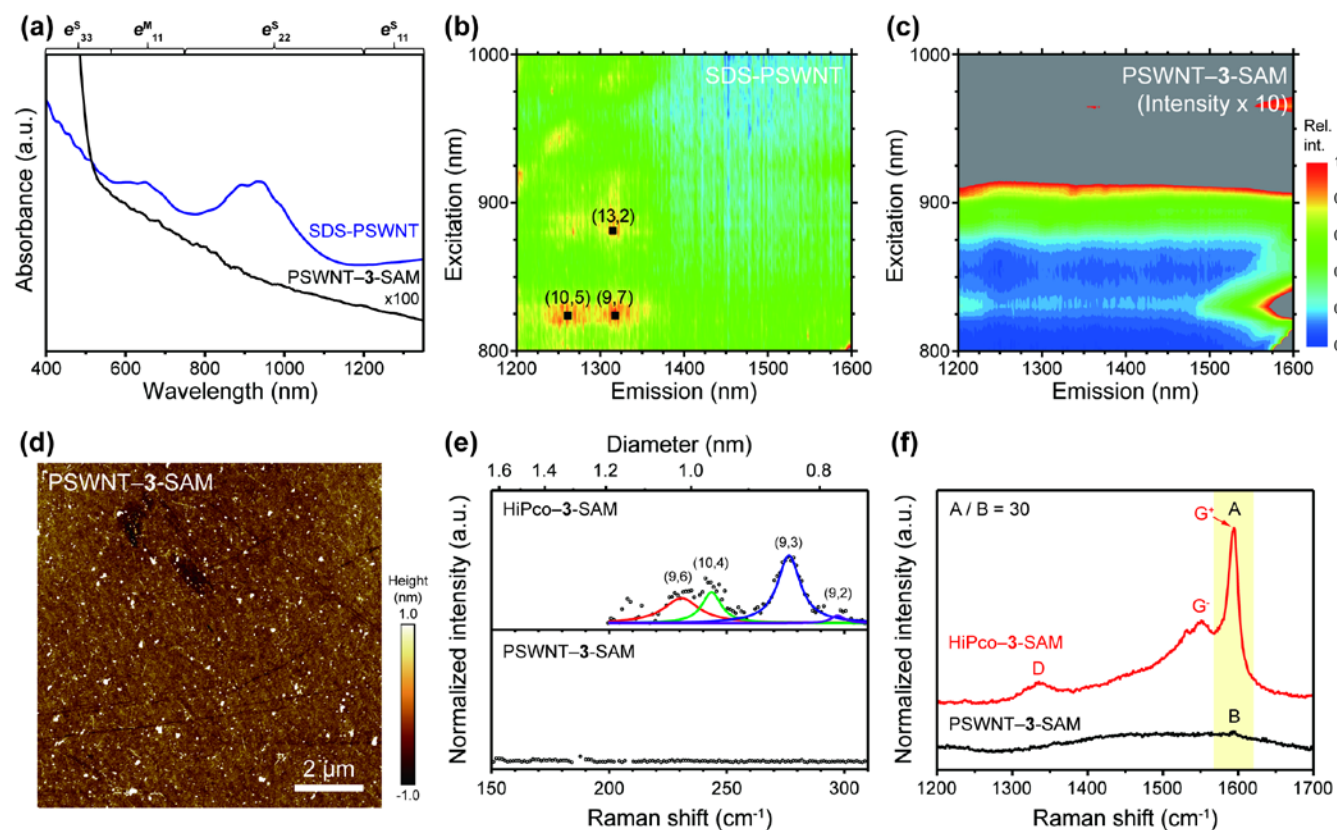


Figure S14. Absorption spectrum changes of 3-SAM with time of dipping into SDS-HiPco dispersion with (a) horizontal dipping without sonication, and (b) vertical dipping with sonication. The spectra were offset by 0.003 for visual clarity.

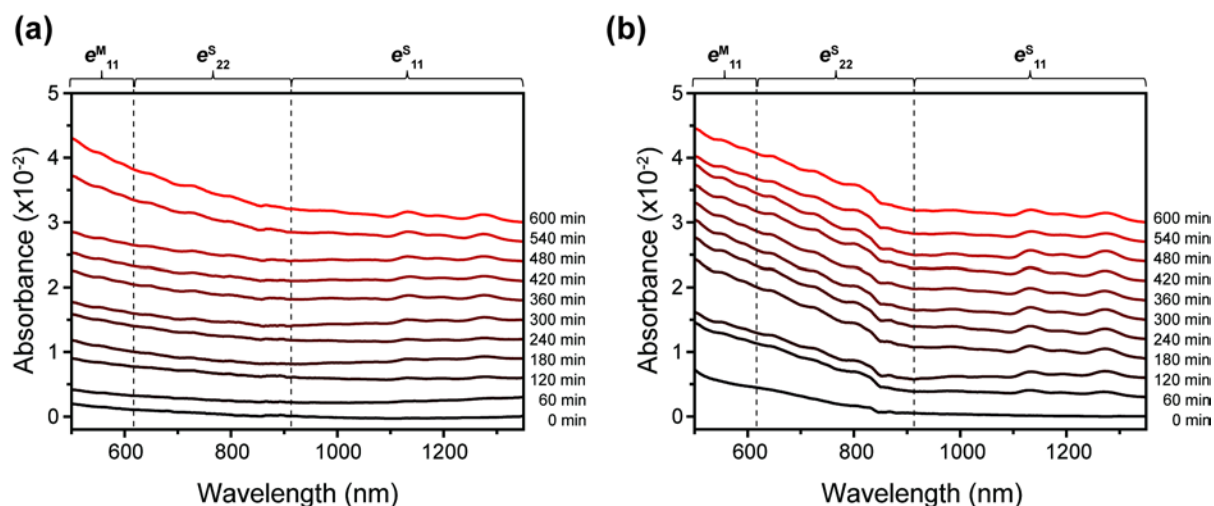


Figure S15. Peak-dependent absorption change of HiPco-3-SAM with dipping time.

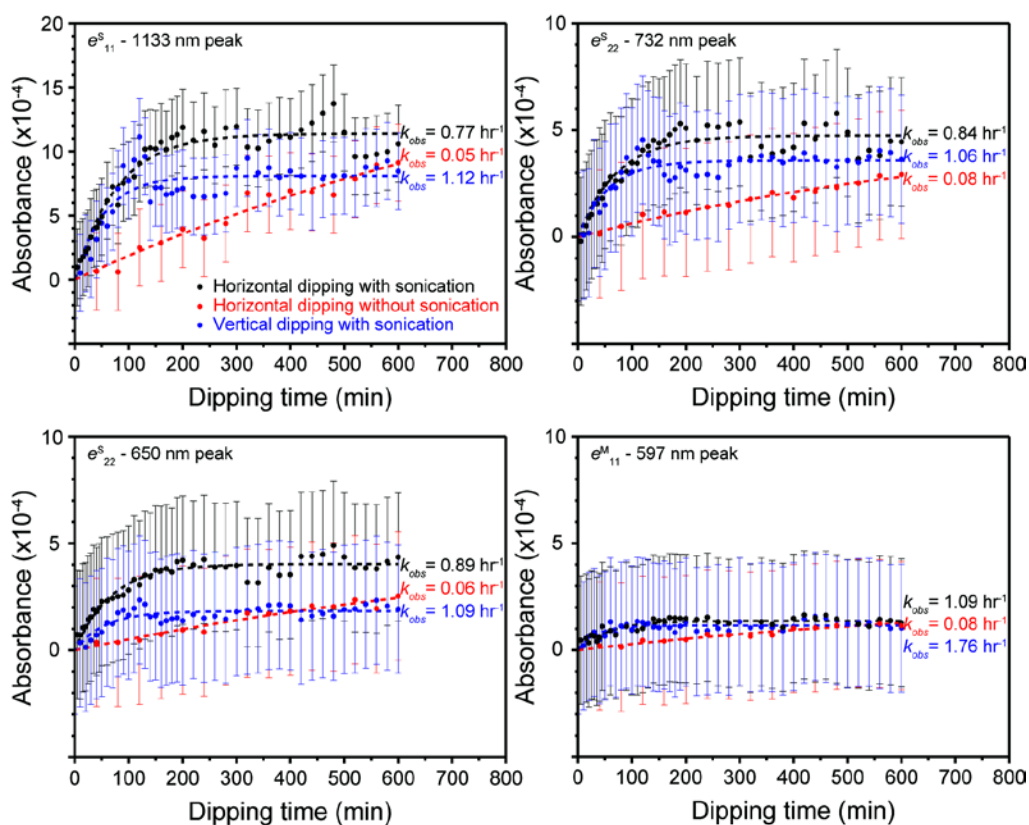
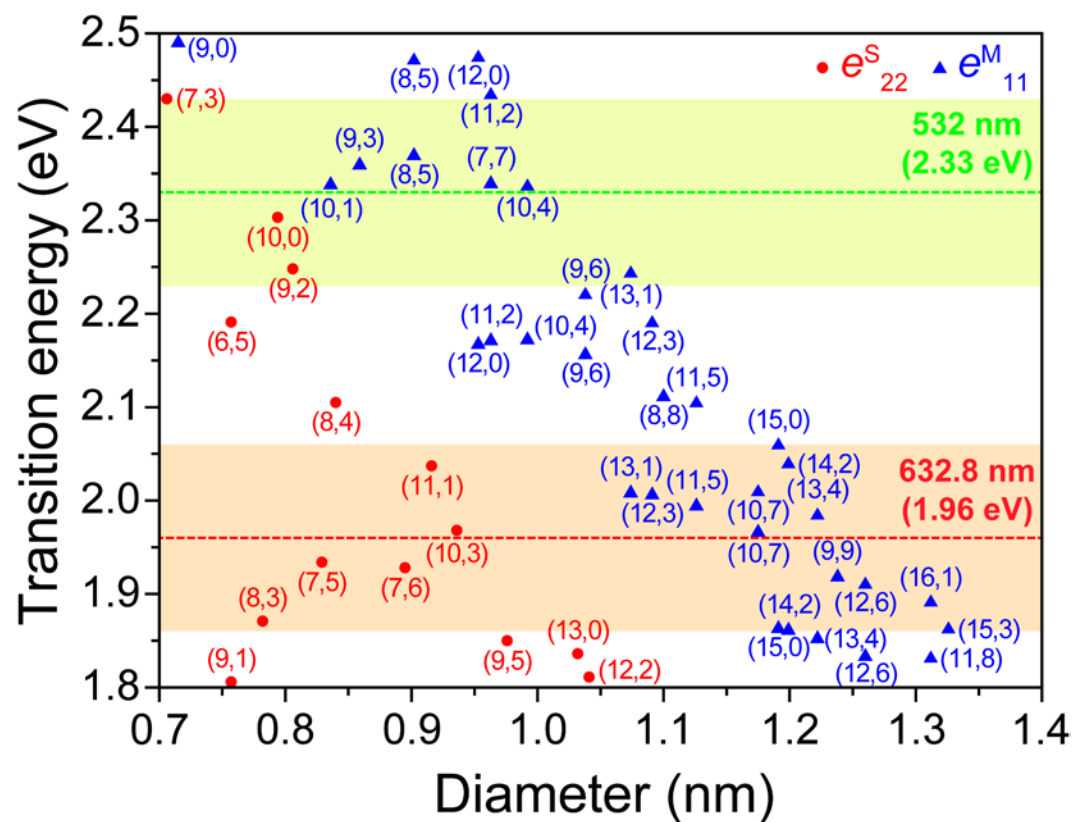


Figure S16. Probed (n, m) species by 532 and 632.8 nm lasers by using a Kataura plot.



Scheme S1. The process to prepare a patterned SAMs alternated by OTS-, and 3-SAMs.

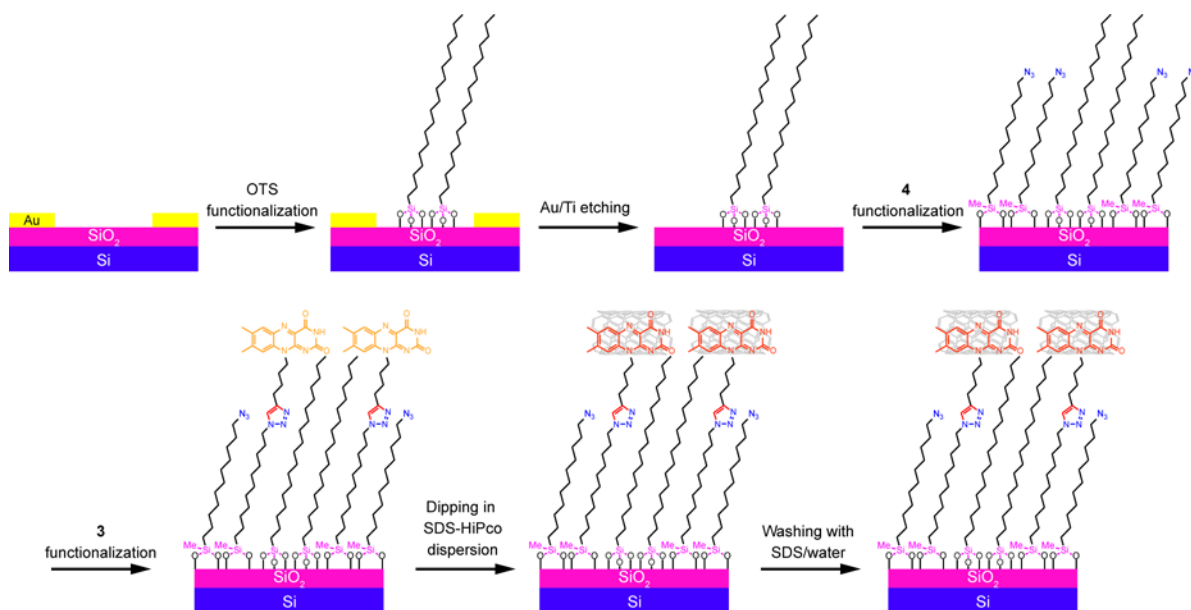


Table S1. PL-based e^S_{11} and e^S_{22} positions and relative PL intensities.

Nanotube Assignment	Diameter	Chiral Angle	HiPco-3-SAM (a)			FMN-HiPco (b)			SDS-HiPco (c)			(b)-(a)		(c)-(a)	
			e^S_{11}	e^S_{22}	Rel. Int.	e^S_{11}	e^S_{22}	Rel. Int.	e^S_{11}	e^S_{22}	Rel. Int.	e^S_{11}	e^S_{22}	e^S_{11}	e^S_{22}
(<i>n,m</i>)	[nm]	[Degree]	[nm]	[nm]		[nm]	[nm]		[nm]	[nm]		[meV]	[meV]	[meV]	[meV]
(6,5)	0.76	27.0	993.5	575.6	0.83	1000.2	581.0	0.96	979.4	568.7	0.75	-8.4	-20.0	18.0	26.1
(8,3)	0.78	15.3	972.0	672.0	0.94	984.1	678.2	0.67	950.8	665.6	0.44	-15.7	-16.9	28.4	17.7
(7,5)	0.83	24.5	1039.0	651.8	0.87	1065.4	657.0	1.00	1023.7	645.0	0.69	-29.6	-15.1	17.8	20.1
(8,4)	0.84	19.1	-	-	-	1144.2	607.9	0.82	1113.8	588.4	1.00	-	-	-	-
(10,2)	0.88	8.9	1076.5	742.4	0.74	1096.5	753.5	0.35	1054.8	734.8	0.53	-21.0	-24.6	23.7	17.3
(7,6)	0.89	27.5	1140.4	651.8	1.00	1162.2	670.3	0.66	1121.9	646.8	0.90	-20.4	-52.5	17.9	14.7
(11,1)	0.92	4.3	1279.0	625.0	0.75	1293.7	626.3	0.30	1266.6	611.7	0.42	-11.0	-4.1	9.5	43.1
(9,4)	0.92	17.5	1129.2	730.0	0.84	1135.7	734.9	0.54	1102.7	718.4	0.62	-6.3	-11.3	26.4	27.4
(10,3)	0.94	12.7	1280.0	643.0	0.83	1292.1	646.9	0.30	1251.3	629.6	0.39	-9.1	-11.6	22.2	41.0
(8,6)	0.97	25.3	1198.3	725.2	0.88	1212.8	738.0	0.56	1175.7	714.6	0.60	-12.4	-29.7	19.9	25.4
(9,5)	0.98	20.6	1272.0	682.5	0.88	1286.6	688.6	0.42	1244.2	674.0	0.48	-11.1	-16.1	21.8	22.9
(8,7)	1.03	27.8	1285.1	733.8	0.85	1314.5	744.5	0.18	1270.7	728.1	0.38	-21.6	-24.3	10.9	13.2
									Average			-15.1	-20.6	19.7	24.5

Table S2. k_{obs} , K' , k_a , k_{aC} , k_d , and k_d/k_{aC} according to optical transitions of HiPco and dipping methods.

Constants	Horizontal dipping without sonication		Horizontal dipping with sonication		Vertical dipping with sonication	
	e^S_{11}					
	1272 nm	1133 nm	1272 nm	1133 nm	1272 nm	1133 nm
k_{obs} (hr^{-1})	0.078	0.053	0.78	0.77	1.11	1.12
K' ($\times 10^{-3}$)	1.86	2.19	1.28	1.14	0.97	0.81
k_a ($\times 10^{-3}$, $\text{mL}/\mu\text{g}\cdot\text{hr}$)	0.18	0.15	1.25	1.10	1.35	1.14
$k_a\text{C}$ ($\times 10^{-3}$, hr^{-1})	0.15	0.11	0.10	0.88	1.08	0.91
k_d (hr^{-1})	0.078	0.053	0.78	0.77	1.11	1.12
$k_d/k_a\text{C}$	537	456	780	876	1030	1233
	e^S_{22}					
	732 nm	650 nm	732 nm	650 nm	732 nm	650 nm
k_{obs} (hr^{-1})	0.076	0.058	0.84	0.89	1.06	1.09
K' ($\times 10^{-3}$)	0.53	0.55	0.47	0.40	0.36	0.18
k_a ($\times 10^{-3}$, $\text{mL}/\mu\text{g}\cdot\text{hr}$)	0.050	0.040	0.49	0.44	0.48	0.24
$k_a\text{C}$ ($\times 10^{-3}$, hr^{-1})	0.040	0.032	0.39	0.35	0.38	0.20
k_d (hr^{-1})	0.076	0.058	0.84	0.89	1.06	1.09
$k_d/k_a\text{C}$	1886	1817	2127	2499	2777	5555
	e^M_{11}					
	597 nm	557 nm	597 nm	557 nm	597 nm	557 nm
k_{obs} (hr^{-1})	0.075	0.076	1.09	0.98	1.76	2.42
K' ($\times 10^{-3}$)	0.24	0.28	0.14	0.35	0.12	0.34
k_a ($\times 10^{-3}$, $\text{mL}/\mu\text{g}\cdot\text{hr}$)	0.023	0.027	0.19	0.43	0.26	1.03
$k_a\text{C}$ ($\times 10^{-3}$, hr^{-1})	0.020	0.021	0.15	0.34	0.21	0.82
k_d (hr^{-1})	0.075	0.076	1.09	0.98	1.76	2.42
$k_d/k_a\text{C}$	4166	3570	7142	2856	8332	2940

Cited references

- (1) Zhang, J.; Chi, Q.; Wang, E.; Dong, S. A Comparative Study on STM Imaging and Electrocatalytic Activity of Different Surfaces Modified with Flavin Adenine Dinucleotide, *Electrochim. Acta* **1995**, *40*, 733-744.