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Isotopic-Induced Variation in the Stability of FMN-Wrapped Carbon Nanotubes

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Abstract

Isotopic, hydrogen-to-deuterium substitution has been an invaluable tool in the characterization of small molecules and biological nanostructures. The natural variability of most inorganic nanomaterials has hindered the use of isotopic substitution to gaining meaningful insights of their structure. The ideal helical wrapping of flavin mononucleotide (FMN) around (8,6)-SWNTs (single-walled carbon nanotubes) is presently utilized to probe isotopic-dependent intermolecular interactions. The facile proton-to-deuterium exchange of the imide group of FMN, enabled us to alter the intermolecular stability of the helix depending on the surrounding solvent (*i.e.* H₂O vs. D₂O). Our studies show that FMN-dispersed (8,6)-SWNTs exhibit greater stability in D₂O as opposed to H₂O. The higher complex stability in D₂O was verified based on: (i) FMN helix replacement with SDBS (sodium dodecylbenzenesulfate); as well as (ii) thermal-, and (iii) pH-induced helix dissociation. This is in agreement with the previously observed stronger amide H-bonding of proteins in D₂O, and to the best of our knowledge, it demonstrates the architectural fidelity of FMN-wrapped SWNTs, which is expected to further enhance the assembly repertoire of carbon nanotubes.

INTRODUCTION

Recent advances in the synthesis and applications of nanostructured materials have intensified the need for advanced metrological characterization. Aside from having to institute techniques with greater measuring accuracy, one also needs to increase the reliability in force determination governing nanoscale interactions. While great advances have been accomplished in force determination between individual species using atomic force microscopy (AFM),^[1] these measurements are not easily translated to cooperative systems involving concerted organization. The ordering of surface-binding agents (herein called “surfactants”) around single-walled carbon nanotubes (SWNTs),^[2,3] monodispersed nanocrystals,^[4,5] graphene,^[6] highly-ordered pyrolytic graphite (HOPG),^[7,8] and other crystalline surfaces,^[9] are typically governed by not only surfactant-nanostructure interactions but also by lateral surfactant organization, where curvature is playing an important role. Gaining a better understanding of these interactions is crucial for the field of self-assembly,^[10] since well-defined interfaces provide ideal interacting modules for future nanoarchitectonics.^[11]

Surfactant thermal desorption have been widely used for the determination of binding strength in rigid nanostructures like zeolites and immobilized nanostructures.^[12,13,14]

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Extending thermal desorption to surfactant-dispersed nanocrystals, nanorods, nanotubes and nanoplatelets in the dilute state, is much more challenging due to nanomaterials aggregation following surfactant desorption. Upon formation, such aggregates tend to produce exothermic peaks that interfere with the endothermic surfactant desorption, rendering the results difficult to interpret. Such challenging task can be alleviated if another surfactant cooperatively takes the place of the desorbed surfactant to prevent nanostructure aggregation. This was recently demonstrated for SWNTs dispersed with low molecular weight flavin mononucleotide, (FMN) surfactant that was cooperatively replaced by another surfactant.^[3] Such surfactant exchange induces a spectral shift in the electronic transitions of the encapsulated nanotube,^[15] providing an ideal probe to quantitatively assess the magnitude of nanotube-surfactant interactions for different (*n, m*) chirality semiconducting nanotubes. Having said this, the question remains whether we can assess and quantify the much finer surfactant-surfactant interactions along with their degree of cooperativity.

In this contribution we illustrate that the surfactant-surfactant interactions at the surface of a nanomaterial can be differentiated via isotropic, hydrogen-to-deuterium substitution. For this, we employed the ideal helical wrapping of FMN around (8,6)-SWNTs, whose lateral stability is intimately coupled to the quadruple H-bonds responsible for forming the isoalloxazine ribbon, shown in Figure 1.^[3,16,17,18] Depending on the surrounding solvent (*i.e.* H₂O *vs.* D₂O), the facile proton-to-deuterium exchange of the imide group enabled us to alter the intermolecular surfactant-surfactant interactions, while keeping the overall 8/1 FMN-dimer helix virtually intact. Such isotopic exchange indicated that FMN-dispersed (8,6)-SWNTs exhibit greater stability in D₂O as opposed to H₂O. This was verified in terms of higher FMN helix stability in D₂O against its: (a) replacement with SDBS (sodium dodecylbenzenesulfate) surfactant exchange; and (b) thermal dissociation, which induces nanotube aggregation. This is in agreement with the previously observed stronger H-bond for N-D⁺···O=C *vs.* N-H⁺···O=C amides. This demonstrates the supreme architectural fidelity of FMN-wrapped nanotubes. Moreover, the controlled thermal and surfactant-exchange dissociation of the FMN helix is expected to further enhance the self-assemble repertoire of carbon nanotube along the lines of DNA and protein nanoarchitectonics.^[19,20,21]

EXPERIMENTAL SECTION

Materials

HiPco single-walled carbon nanotubes (SWNTs) were purchased from Unidym (with the lot number of R0513) and used without further purification. Riboflavin 5'-monophosphate sodium salt hydrate (FMN) 73–79%, and sodium dodecylbenzenesulfonate (SDBS) (technical grade) were purchased from Sigma-Aldrich and used as is. Deuterium oxide (D₂O) 99.8%, deuterium chloride (DCI) (20 wt.% solution in D₂O), sodium deuteroxide (NaOD) (40 wt.% solution in D₂O) and hydrochloric acid, (1N standard solution) were acquired from Acros. Sodium hydroxide solution (1N Certified) was purchased from Fisher Chemical.

Characterization

Steady state fluorescence spectroscopy measurements were performed on a Jobin-Yvon Spex Fluorolog 3–211 spectrofluorometer equipped with a PMT NIR detector. Both excitation and emission spectra were collected with a 3 nm step size and their light intensities were corrected against instrumental variations using the Spex Fluorolog sensitivity correction factors. Steady state UV-Vis-NIR absorption spectroscopic measurements were obtained with a Perkin-Elmer Lambda 1050 UV-Vis-NIR spectrometer. pH measurements were performed using an Accumet Model #15 pH meter.

Preparation of H₂O or D₂O dispersions of FMN-wrapped SWNTs

Aqueous dispersions of SWNTs were prepared by adding 100 mg of HiPco SWNTs and 1.000 g of FMN to 100 mL of H₂O (D₂O). The mixture was bath sonicated for 1h, followed by tip sonication at 50% power for 4h, (Cole Parmer Ultrasonic Processor, 300 W), and ultracentrifuged at 100 kg for 10h (Beckman, SW28 rotor) to remove the majority of nanotube bundles and large aggregates. The resulting dispersion has a clear, dark greenish appearance and is mostly composed of FMN-wrapped SWNTs. This was further diluted in 1-to-3 v/v ratio with either H₂O or D₂O containing the same starting concentration of FMN, followed by a 30 min bath sonication to ensure that most FMN-wrapped SWNTs are individualized.

pH titrations of H₂O or D₂O dispersions of FMN-wrapped SWNTs

HCl and NaOH solutions with concentration of 0.5 N were prepared by 50% v/v dilution of a standard 1N solutions with deionized water. Similarly, 0.5 N DCl and NaOD solutions were prepared from their 20 wt.%, and 40 wt.% solutions by appropriate dilution with D₂O. Acid or basic titrations from the neutral FMN-wrapped SWNT dispersions were performed by the appropriate addition of acid or base, followed by 5 min bath sonication to ensure complete pH equilibration. PL spectra were collected at each addition of acid or base (excitation at 744 and 741 nm for D₂O and H₂O dispersions of FMN-wrapped-SWNTs, respectively), along with measuring the resulting pH value.

FMN-to-SDBS surfactant exchange in H₂O or D₂O dispersions

Microliter portions of 0.1 N SDBS solution in H₂O or D₂O were added to 5 ml of the corresponding starting H₂O or D₂O dispersions of FMN-wrapped SWNTs, and the mixture was gently hand-shaken to prevent any bubble formation, prior to collecting its PL spectra (excitation at 715 nm for both D₂O and H₂O dispersions). The PL titration curves were fitted with the sigmoidal Hill equation,^[22] to obtain the fitted K_a (mid-point) and γ (sigmoidal breadth) values. The K_a value is proportional to the binding strength of FMN to the nanotube, against SDBS replacement, while the γ value is inversely proportional to the cooperativity of this exchange.

Melting point measurements of H₂O or D₂O dispersions of FMN-wrapped SWNTs

A small amount (*ca.*10 ml) of as prepared H₂O or D₂O dispersions of FMN-wrapped SWNTs were transferred to a sample vials and were incubated for 5 min in an oil bath at a given temperature, before cooling down at room temperature, where its luminescence were measured (excitation at 744 and 741 nm for D₂O and H₂O dispersions of FMN-wrapped-SWNTs, respectively). The resultant PL intensities were normalized against the starting PL intensity at 25 °C. The midpoint of each PL intensity decay, herein reported as the “melting point” (m.p.) of the FMN helix, was obtained by sigmoidal Boltzmann fitting.^[23]

RESULT AND DISCUSSION

Hydrophobic interaction play a key role in various molecular organization in aqueous media, such as cell membrane assembly, protein folding and DNA hybridization.^[24,25,26,27] The formation of extended H-bonded networks between adjacent water molecules, produces ordered H₂O organization with substantial enthalpic stabilization in the liquid phase.^[28,29,30,31,32] Hydrophobic interactions and the poor solubility of non-polar molecules in water stems from the local destruction in H-bonding structure, that the insertions of these molecules inflict to the water lattice. This leads to the spontaneous rearrangement of water molecules in a cage-like structure around the solute.^[29] This cage-like structure, if regular, can lead to the formation of slightly stronger H-bonding, similar to air-water interfaces that exhibit substantial surface tension.^[32] Consequently, hydrophobic stabilization stems from

the energy minimization of the total surface exposed to water as two or more molecules come together to reduce the local water restructuring.^[31] This explains the profound aggregation tendency of pristine single-walled carbon nanotubes (SWNTs) in aqueous media.^[33] Surfactants with appropriate structure to accommodate the extreme nanotube curvature have the ability to individualize SWNTs *via* introducing two additional interfaces with hydrophobic and hydrophilic interactions at opposite sides of the surfactant.^[34] More recently, bile salts have led to improved stability of nanotube-surfactant suspensions.^[35] A plausible explanation for the improved stability of such complexes is that their water cage attain greater long-range order.^[29b] Along these lines, single-stranded (ss)-DNA and flavin mononucleotide (FMN) provide the planarity of bile salts as well as improved intermolecular interactions with both nanotubes (*via* charge transfer (CT)) and surfactant-surfactant stabilization (*via* intermolecular H-bonding).^[2-3] In both cases, the formation of ordered surfactant assemblies has the potential to also increase the long-range order of the surrounding water cage. This begs the question whether solvent isotopic effects show any variation in the stability of FMN-wrapped nanotubes.

Despite the physical similarities of H₂O and D₂O, their influence on living systems is strikingly different.^[36] D₂O is highly toxic and even lethal at high concentrations for most living organisms. These two solvents possess some key different properties, which can greatly influence the organization of complex biostructures.^[37,38,39,40] For example, the hydrophobic interactions are stronger in D₂O than in H₂O. This phenomena is attributed to the fact that the OH bond length in H₂O is *ca.* 3% longer than that of O-D, while H-bonding in D₂O is *ca.* 4% shorter than that in H₂O.^[41] This leads into a 5% stronger H-bonding in D₂O as opposed to H₂O.^[39] Such increased strength is related to the higher mass of deuterium, which lowers the zero-point vibrational energy of the intermolecular mode of its highest frequency.^[38,42]

Since hydrophobic interactions and H-bonding are stronger in D₂O, as opposed to H₂O, the helical wrapping of FMN around pristine SWNTs provides an ideal system to study the weak surfactant-surfactant interactions and hydrophobic effects on nanomaterials using hydrogen-to-deuterium substitution. Exchanging of hydrogen with deuterium in imides and alcohols are fast (typically in millisecond and second time range, respectively).^[43,44] Consequently, following a 4 hr. sonication of SWNTs in a D₂O solution of FMN, an exchange of all mobile hydrogens to deuterium atoms is expected. Figure S1 in the Supplemental Information Section, illustrates the deuterium-replaced hydrogens which are namely: (i) Isoalloxazine imide N-H to N-D; and (ii) Phosphate and *D*-ribityl O-H groups to O-D. Recent isotopic studies on proteins indicate that N-D is 0.03 Å shorter than N-H, and the N-O distance (N-H...O=C) are 0.02 ± 0.02 Å shorter in D₂O as opposed to H₂O.^[45] This is expected to correspondingly decrease the neighboring isoalloxazine distances and possibly modify the stability of the FMN helix around a given SWNT.

The close intermolecular proximity that the isoalloxazines moieties of FMN need to attain in order to realize a stable self-assembled ribbon around SWNTs requires appropriate curvature. This curvature ensures minimal repulsion from the neighboring two isoalloxazine hydrogens (at C9 and one of the hydrogens of C-8 methyl group) on the two C1' hydrogen atoms of the *D*-ribityl side group that hover above the isoalloxazine plain (Figure 1a&c).^[18] In turn, this curvature requirement naturally selects SWNTs with diameter from 0.76 to 1.17 nm.^[3] The optimum wrapping curvature for an 8/1 flavin helix is realized for (8,6)-SWNTs with diameter of 0.96 nm. This nanotube produces the most stable FMN/SWNT complex along with naturally enhancing its enrichment, as shown from the photoluminescence excitation (PLE) maps of Figure 2.

Upon closer examination of the PLE maps of FMN-wrapped nanotubes in both H₂O and D₂O, it becomes apparent that both solvents disperse the similar (*n, m*)-sem-SWNTs, mostly composed of (8,6), (9,4), (9,5), (7,6), (8,4), (7,5), (8,3) and (6,5). Among the two solvents, the (8,6)-SWNT appears to be more enriched in D₂O, judging from the substantial PL intensity of (6,5) and (8,4) in H₂O. Moreover, the nanotube individualization appears more enhanced in D₂O as opposed to H₂O, based on the sharpness of the D₂O PLE map, which exhibits lesser EET (excitation energy transfer) cross peaks.^[46] Apart from this, both H₂O and D₂O behave similarly, which justify us focusing on the strongest FMN-wrapped nanotube complex (*i.e.* (8,6)-SWNT)^[3] for the rest of this contribution, in order to reveal finer isotopic differences.

Figure S2 and S3 illustrate the superimposed luminescence and excitation scans for (8,6)-SWNTs (*i.e.* horizontal and vertical traces of Figures 1a&b). Both (8,6) E_{11}^S emission maxima are very close to each other (1213.2 and 1212.5 for H₂O and D₂O, respectively), with full-width at half maximum (FWHM) for H₂O (48.0 nm) slightly larger than D₂O (46.4 nm) (Figure S2). This pattern is reversed for the (8,6) E_{22}^S peaks in terms of excitation maxima, while the H₂O's FWHM (30.9 nm) is still greater than D₂O (29.3 nm) (Figure S3). Such E_{11}^S , E_{22}^S maxima inversion trend has been observed before,^[3] and is consistent with FMN helical wrapping of SWNTs.^[18] The slightly redshift in E_{11}^S PL emission of (8,6)-SWNTs in H₂O than D₂O is currently believed to originate mainly from the higher dielectric constant of H₂O vs. D₂O,^[47] and to a lesser extend from charge transfer differences between the two helices. Having said this, the higher FWHM values for both (8,6) E_{11}^S and E_{22}^S transitions in H₂O suggest that the 8/1 FMN helix possess greater inhomogeneity along the length of the nanotubes,^[16] as opposed to D₂O, which concurs with the lesser (8,6)-SWNT enrichment in H₂O (apparent from Figure 1, S2 & S3).^[3]

The slightly different pH values for H₂O and D₂O prompted us to also look into ionization variability of the two species and their influence to the luminescence intensity of the surrounded (8,6)-SWNT. Figure 3 illustrate the normalized photoluminescence intensity of (8,6)-SWNTs as a function of pH or pD, in conjunction with their acid/base titration curves. This was performed by titrating with acid and base the individualized FMN-wrapped nanotube dispersions, whose starting pH was 6.26 and 6.83 for H₂O and D₂O, respectively. Here, it is important to stress that all pD values measured by pH meter have been corrected based on Eq. 1,^[48] and pK_a values for deuterated FMN are calculated based on Eq. 2.^[49]

$$\text{pD}_{\text{corrected}} = \text{pH}_{\text{experimentally measured}} + 0.4 \quad (1)$$

$$\text{pK}^D = \text{pK}^H + \Delta \text{pK}^{D-H}, \quad \Delta \text{pK}^{D-H} = 0.076 \text{pK}^H - 0.05 \quad (2)$$

The pH titration curves provides us for the most part a snapshot of the different ionization states of the phosphate group (termed as H₂(FMN), H(FMN)⁻ and (FMN)²⁻) at the tail end of the *D*-ribityl side chain of FMN, and to a lesser extend the ionization of the isoalloxazine imide hydrogen (defined as (FMN)³⁻), which takes place at higher pH values. Recent studies in the acidity constants of FMN in aqueous solutions indicate the following three pK_a values for the ionization equilibriums of Eq. (2–4).^[50]

The dashed lines in Figures 3a&b indicate the two equivalent points (EQP), where the FMN's phosphate group can be found in a single ionization state (*i.e.* $\text{H}(\text{FMN})^-$ and $(\text{FMN})^{2-}$ for EQP₁ and EQP₂, respectively). Maximum PL intensity is observed for both H₂O and D₂O between these two points, suggesting that three O⁻ charges every two phosphate groups is the ideal charge repulsion for maximum FMN helical stability of (8,6)-SWNTs. In the lower pH range, the luminescence of (8,6)-SWNTs drops substantially, due to the lack of adequate charge repulsion from the phosphate groups to prevent nanotube aggregation. The gradual PL intensity drop in the range of pH or pD of 7 to 8.5 originates from excessive charge repulsion of the phosphate groups. In this region, the FMN helices bear more than three negative charges per two phosphate groups (nearly four charges), which destabilize the helix *via* excessive charge repulsion. In the higher pH range (greater than 10), the loss of PL intensity is more dramatic and it is clearly associated with the destruction of the FMN helix due to imide proton ionization. Such ionization disrupts the H-bonded ribbon (Figure 1a) by inhibiting the H-bonding formation among the adjacent isoalloxazine rings.

Figure 3c contrasts the titration curve differences between H₂O and D₂O. To the first approximation, these results obey the well-accepted formula of Eq. 1 (for the titration curves) and Eq. 2 (for the two equivalent points EQP₁ and EQP₂).^[51] On the other hand, the higher PL stability in the region of 6–12 (Figure 4d) indicate that the deuterated FMN helix (Figure S1) is more stable against phosphate charge repulsion and imide dissociation, as opposed to the normal FMN helix. This is the first indirect indication of the higher FMN helix stability in D₂O as opposed to H₂O, which is agreement with the enrichment and linewidth results of Figures 2 and S2 & S3, respectively.

The cooperative replacement of FMN with sodium dodecylbenzenesulfate (SDBS) has proven an invaluable tool in the determination of binding strength of the flavin helix around various (*n, m*)-SWNTs.^[3] Figure 4a illustrates the FMN-to-SDBS replacement of (8,6)-SWNTs in H₂O and D₂O, with the individual PL traces shown in Figures S4 and S5, respectively. The stability of the FMN helix is expressed in terms of the amount of SDBS required for replacing FMN with SDBS. This surfactant exchange also prevents the nanotubes from aggregating, thereby allowing them to be used as an internal probe to assess replacement dynamics. This replacement causes a significant blueshift in both PL and PLE maxima, *ca.* 31 and 28 nm shifts for the E_{11}^S transition for H₂O and D₂O, respectively along with a common 26 nm blueshift for the E_{22}^S transition of (8,6)-SWNTs.^[3] This enables us to selectively monitor the particular nanotube species, which in this case is (8,6)-SWNTs.^[3] The inflection point (K_a , shown as stars in Figure 4a) and $1/\gamma$ (γ = the width of the sigmoidal transition, 2.78 and 3.14 mmol of SDBS for H₂O and D₂O, respectively) provide the binding strength and cooperativity of the FMN helix around (8,6)-SWNTs. The results of Figure 4a provide the first solid proof that the deuterated FMN helix binds stronger onto (8,6) nanotubes as opposed to normal FMN. Moreover, the significant higher cooperativity of the FMN-to-SDBS replacement of the deuterated FMN helix verifies its higher spatial uniformity along the nanotube backbone.

The close analogy of the double stranded *ds*-DNA hybridization geometry to the H-bonded stabilized FMN ribbon (Figure 1), begs the question whether thermal denaturation experiments^[52] can also be used to verify the higher binding stability of the deuterated FMN helix. Here, the progressive temperature increase is expected to “melt” or dissociate the H-bonds of the FMN-helices and induce subsequent nanotube bundling and precipitation. This can be readily witnessed by monitoring the loss of the given (*n, m*)-sem-SWNT PL

intensity. Figure 4b illustrates the thermal dissociation results of FMN-wrapped (8,6)-SWNT in H₂O and D₂O, with the individual PL traces shown in Figure S6 and S7, respectively. A nearly 10 °C difference is witnessed between the “melting points” of the two species. This finding is in agreement with the FMN-to-SDBS replacement results, verifying beyond reasonable doubt that the deuterated flavin helix is substantially more ordered than the normal one. Unfortunately, the non-reversible nature of nanotube aggregation preclude us to make solid conclusions on the cooperativity of thermal dissociation of the FMN helix, which gives us a clue of the spatially uniformity of these helices.

The structural similarity of the normal and deuterated FMN helices around the same (*n*, *m*)-SWNT species (*i.e.* (8,6)), involves for the most part similar π - π stacking interactions. Consequently, differences in H-bonding between N-H $\cdots$ O=C and N-D $\cdots$ O=C are expected to play a key role in the stability of the normal and deuterated helices.^[45] The 5% stronger H-bonding in D₂O as opposed to H₂O,^[39] along with the average 0.02 ± 0.02 Å shorter N-O distances in proteins dissolved in D₂O *vs.* H₂O,^[45] supports a closer isoalloxazine-isoalloxazine packing in D₂O as opposed to H₂O. In analogy with many polymeric systems, decrease in H-bonding distance increases their melting points.^[37,53] Correspondingly, the shorter H-bonds in D₂O concurs with the increased FMN-to-SDBS replacement transitions and thermal denaturation results of Figure 4a&b. Moreover, the increased deuterium attraction is expected to slightly shrink the width of the H-bonded ribbon (Figure 1a) and possibly facilitate an easier lateral packing of FMN along the length of the nanotube (Figure 1c). Such improved lateral packing might also enhance the surrounding water organization around the helix. This in conjunction with the slightly higher melting point and dipole moment of D₂O *vs.* H₂O,^[54,55] could account for the improved thermal stability and structural uniformity of FMN-wrapped (8,6)-SWNTs in D₂O. Moreover, in accordance with a previous study,^[16] the narrower PL linewidth and significantly stronger emission of (8,6)-SWNTs in D₂O *vs.* H₂O (Figure S2) offer additional credence for the improved structural uniformity (*i.e.* lateral packing) of the FMN helix in D₂O.

CONCLUSIONS

The ordered helical wrapping of FMN around (8,6)-SWNTs provides an ideal system to investigate isotopic-dependent intermolecular interactions in coatings, wrapped around nanomaterials with high uniformity. With the help of: (i) spectroscopic investigations; (ii) FMN helix replacement with a normal surfactant (*i.e.* SDBS); and (iii) pH as well as thermal-induced helix dissociation studies, the higher stability of the FMN helix in D₂O *vs.* H₂O is demonstrated. This is attributed to the stronger isoalloxazine H-bonding in D₂O along with improved lateral packing of the FMN helix in the deuterated medium. A number of profound ramifications can be extracted from the results of this study. First and foremost, isotopic substitution can be used to study the internal stability of nanostructured systems involving complex self-assembly organizations. Such isotopic substitutions can help us pinpoint forces that affect nanoscale properties with atomic and even sub-atomic resolution. Clearly, the computation challenges of this and relative systems are formidable, but with careful consideration one might be able to successfully tackle them. Linking the present results with computation understanding as well as providing future isotopic experiments based on infrared spectroscopy and neutron scattering holds enormous promise for advancing nanometronics of carbon nanotubes and related nanomaterials. Moreover, these studies can provide increased insight to the field of self-assembly and help define well-controlled interfaces for future nanosized architectures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Organization structure of flavin mononucleotide (FMN) around (8,6)-SWNTs. **(a)** Quadruple H-bonding stabilize the isoalloxazine ribbon that orderly wraps itself around the (8,6)-SWNT **(b)**, while the *D*-ribityl phosphate side groups providing aqueous solubilization **(c)**. C, H, N, O and P are illustrated as grey, white, blue, red and pink spheres, respectively.

Figure 2. Photoluminescence excitation (PLE) maps of FMN-wrapped SWNT dispersed in H₂O (a) and D₂O (b). Samples were centrifuged at 100 kg to increase nanotube individualization.

Figure 3.

Normalized photoluminescence intensity of (8,6)-SWNTs (left ordinate) and acid/base titration (right ordinate) curves as function of pH or pD, for H₂O (a) and D₂O (b) dispersions of FMN-wrapped nanotubes, respectively. The excitation wavelength for the H₂O and D₂O dispersions are 741 and 744 nm, respectively, with a common 1212 nm emission wavelength. Superposition of titration (c) and normalized PL intensity (d) curves as a function of pH or pD.

Figure 4.

(a) FMN-to-SDBS surfactant exchange titration in H₂O and D₂O monitoring the photoluminescence intensity of (8,6)-SWNTs at their SBDS position (with a common 715 nm excitation and 1182 and 1186 nm emission for H₂O and D₂O, respectively). (b) Normalized photoluminescence intensity of FMN-wrapped (8,6)-SWNTs in H₂O and D₂O dispersions as a function of temperature (excitation wavelength for the H₂O and D₂O dispersions are 741 and 744 nm, respectively, with a common 1212 nm emission wavelength).