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Brightly Fluorescent Single-Walled Carbon Nanotubes via an Oxygen-Excluding Surfactant Organization

Sang-Yong Ju,1 William P. Kopcha,2 Fotios Papadimitrakopoulos1,2,*

Attaining high photoluminescence quantum yields for single-walled carbon nanotubes (SWNTs) in order to broaden their optoelectronics and sensing applications has been a challenging task. Among various nonradiative pathways, sidewall chemisorption of oxygen provides a known defect for exciton quenching through nanotube hole doping. We found that an aliphatic (dodecyl) side group, termed FC12, imparts considerable individualization in toluene and other aromatic solvents (i.e., o-xylene and benzene). In addition, the tight self-organization of FC12 around SWNTs leads to an effective exclusion of oxygen that affords quantum yields as high as 20%.

Flavin mononucleotide (FMN), a common redox cofactor related to vitamin B2, was recently shown to self-organize around SWNTs through a helical conformation (18). Such helical wrapping (Fig. 1B) could result from two sets of self-recognition H-bonds that “stitch” the neighboring FMN moieties into a continuous helical ribbon (Fig. 1A), the concentric π-π interaction of the isoalloxazine ring with the underlying graphene sidewalls (Fig. 1B), and a soluble d-ribityl phosphate side group, which imparts effective solubilization in aqueous media. In an effort to broaden flavin-based dispersion in organic solvents, we synthesized an isoalloxazine derivative with an aliphatic (dodecyl) side group, termed FC12. The synthetic route of FC12 involves two facile steps with an overall yield of ~35% (19). FC12 dispersions of CoMoCAT (Co-Mo bimetallic catalyst synthesized) SWNTs (20) were obtained by sonicating 1 mg of FC12, 1 mg of SWNTs, and 4 ml of various solvents for 4 hours at 300 W. The mixture was centrifuged for 20 min at 10,000g, which eliminated visible SWNT bundles in various solvents [i.e., benzene, toluene, o-xylene, ethylacetate, tetrahydrofuran (THF), pyridine, acetone, and N,N-dimethyl formamide (DMF)]. Table 1 summarizes the physical properties of these solvents as a function of dielectric constant (ε). SWNT photoluminescence was observed for only some of these solvents: benzene, toluene, o-xylene, ethylacetate, THF, and acetone (see below).

PLE maps for benzene, toluene, ethylacetate, and acetone show that the photoluminescence intensity (~315,000 counts) of FC12 (6,5)-SWNTs in toluene dispersion is 15 to 20 times

1Nanomaterials Optoelectronics Laboratory, Polymer Program, University of Connecticut, Storrs, CT 06269, USA.
2Department of Chemistry, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA.
*To whom correspondence should be addressed. E-mail: papadim@mail.ims.uconn.edu
that for other solvents (see maximum intensity in the bottom of each panel in Fig. 2; table S1 lists the relative photoluminescence intensities as a function of nanotube species, diameter, and chiral angle). In all PLE maps, all intensity maxima from the observed first ($E_{11}^1$) and second ($E_{22}^2$) electronic transitions of semiconducting SWNTs are similarly redshifted as in the case of FMN (18). The similar $E_{11}^1$ and $E_{22}^2$ redshift trend in organic solvents, as in the case of FMN in H$_2$O (i.e., 15 to 51 nm for $E_{11}^1$ and 23 to 71 nm for $E_{22}^2$), is in agreement with the tight organization of flavin around SWNTs (18). Figure S2 plots the relative photoluminescence intensity of Fig. 2, B to D, as a function of nanotube diameter $d$. With the exception of (7,5)-SWNTs, which are more abundant in toluene, the relative photoluminescence intensities of the observed nanotube species do not change appreciably with $d$. However, the average photoluminescence full width at half-maximum (FWHM) values of all nanotube species in the solvents with low dielectric constant (i.e., 26 and 27 meV for benzene and toluene, respectively) are significantly less than those in the high-dielectric solvents (i.e., 39 and 45 meV for ethylacetate and acetone, respectively) (table S1). The larger FWHM and lower photoluminescence intensities indicate either large inhomogeneity in FC12 functionalization, or a greater degree of bundling than in the benzene and toluene dispersions, or both.

Tan et al. (12) reported that SWNT aggregation enhances exciton energy transfer (EET) between SWNTs within bundles, where excitation of large band gap tubes leads to emission from SWNTs with smaller band gaps. Such spectral features are easily discernible for species with high concentrations, as in the case of (6,5) and (7,5) for CoMoCAT SWNTs (20). The red arrows in Fig. 2, A to D, indicate such an EET feature between (6,5)- and (7,5)-SWNTs. When normalized to the PLE intensity of (7,5)-SWNTs, the (6,5) → (7,5) EET feature from the benzene and toluene is smaller than those seen in ethylacetate and acetone, by a factor of 2 to 3 (fig. S3).

This result provides an initial indication that SWNT individualization in toluene is one of the reasons for the higher photoluminescence intensity and narrower peaks.

Figure 3A illustrates the corresponding visible–near infrared (Vis-NIR) spectra of FC12-dispersed SWNTs in acetone, ethylacetate, and toluene. The toluene absorption spectrum shows sharper peaks that are shifted to higher energies with respect to those of ethylacetate and acetone, as well as a nearly flat baseline. Note that the three absorption curves in Fig. 3A are not offset with respect to each other; rather, they reside on a power-law background ($\alpha \lambda^b$, where $\lambda$ is the wavelength and $a$ and $b$ are fitted parameters) (19, 21). In addition, the $E_{11}^1/E_{22}^2$ ratio of (6,5)-SWNTs, ~6, is the highest reported thus far, with DNA-wrapped (22), PFO-wrapped (16), and sodium dodecyl benzene sulfonate (SDBS)–dispersed (23) SWNTs showing $E_{11}^1/E_{22}^2$ ratios of 3, 3.5, and 3.5, respectively for (6,5)- or (7,5)-SWNTs. Moreover, the (6,5) $E_{11}^1/E_{22}^2$ ratio is ~6

![Fig. 1. (A) Top view of isalloxazine moieties of FC12 wrapped in a 7/1 helical pattern. Red dotted lines and green spheres depict the intermolecular H-bonding between neighboring isalloxazine moieties and the positions of the solubilizing side chains (undecyl), respectively. Color code for atoms: gray, carbon; white, hydrogen; blue, nitrogen; red, oxygen. (B) Side view illustrates the tight 7/1 helical wrapping of FC12 around (6,5)-SWNTs, which greatly interferes with the presence of a chemisorbed oxygen species (i.e., 1,4-endoperoxide and its van der Waals radii illustrated in purple). (C)](Image)

### Table 1. Quantum yield values for (6,5)-SWNTs as a function of solvent dielectric constant ($\varepsilon$), H-bonding nature, and solubility values for FC12 and lumiflavin.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Photoluminescence activity</th>
<th>Quantum yield of (6,5)-SWNTs (%)</th>
<th>$\varepsilon$</th>
<th>H-bonding capability</th>
<th>Lumiflavin solubility (µg/ml)</th>
<th>FC12 solubility (mg/ml)</th>
<th>Max. $E_{11}^1$ absorption</th>
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<tbody>
<tr>
<td></td>
<td>Sample</td>
<td>Individual</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td>Yes</td>
<td>5</td>
<td>10</td>
<td>2.3</td>
<td>P</td>
<td>4.4</td>
<td>0.31</td>
</tr>
<tr>
<td>Toluene</td>
<td>Yes</td>
<td>11</td>
<td>20</td>
<td>2.4</td>
<td>P</td>
<td>4.3</td>
<td>0.23</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Yes</td>
<td>8.7</td>
<td>16.9</td>
<td>2.5</td>
<td>P</td>
<td>5.9</td>
<td>0.25</td>
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<tr>
<td>Ethylacetate</td>
<td>Yes</td>
<td>0.024</td>
<td>0.4</td>
<td>6</td>
<td>M</td>
<td>14.1</td>
<td>0.51</td>
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<tr>
<td>THF</td>
<td>Yes</td>
<td>0.07</td>
<td>0.1</td>
<td>7</td>
<td>M</td>
<td>46.2</td>
<td>11.03</td>
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<tr>
<td>Pyridine</td>
<td>No</td>
<td>—</td>
<td>—</td>
<td>12.5</td>
<td>M-S</td>
<td>528.7</td>
<td>70.38</td>
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<td>Acetone</td>
<td>Yes</td>
<td>0.08</td>
<td>0.2</td>
<td>21</td>
<td>M</td>
<td>53.9</td>
<td>1.81</td>
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<td>DMF</td>
<td>No</td>
<td>—</td>
<td>—</td>
<td>39</td>
<td>M-S</td>
<td>316.7</td>
<td>22.87</td>
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<tr>
<td>D$_2$O†</td>
<td>Yes</td>
<td>0.08</td>
<td>0.8</td>
<td>79</td>
<td>S</td>
<td>—</td>
<td>—</td>
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</table>

*P, poor; M, moderate; M-S, moderate-strong (32). †FMN-dispersed SWNTs in D$_2$O.
only for toluene, dropping to ~3.5 and 4 for ethylacetate and acetone FC12 dispersions, respectively. Because the $E_{11}^S$ transitions are more susceptible to doping-induced bleaching than are the $E_{22}^S$ transitions (9), larger $E_{11}/E_{22}$ ratios are indicative of a more pristine nature for the SWNTs.

A close-up of the toluene $E_{11}^S$ spectral range, along with peak deconvolution based on the PLE-observed SWNTs, is shown in Fig. 3B. The background-subtracted absorption spectrum (circles) was deconvoluted with a multiplicity of Lorentzian peaks, where their maxima were allowed to vary 1 to 2 nm from the corresponding PLE-derived position (table S1) along with unrestricted FWHM (19). The NIR spectra were adequately described by a simple summation of the individual $(n,m)$-SWNTs observed in the corresponding PLE map of Fig. 2B. This one-to-one correlation between photoluminescence and absorption spectra indicates profound individualization for all observed nanotubes. With the exception of (7,6)-SWNTs, whose FWHM coincides with H$_2$O absorption, the FWHM values of all nanotubes range from 12 to 25 meV, with an average of 18 meV (22 meV for weighted average) (table S2). Comparison of these results with previously reported FWHM absorption values for DNA-wrapped nanotubes (18 to 24 meV) (22) and PFO-dispersed nanotubes (19 to 20 meV) (16) provides additional support for the idea that the helical wrapping of FC12 affords a highly uniform environment around these SWNTs (24).

To assess the deconvolution fidelity of Fig. 3B, we compared the percent abundance obtained by absorbance (Fig. 3B) and PLE intensities (table S2). The diameter ($d_i$), modality [mod($n$-$m$,3) = 1 or 2], family (2$n$+$m$ = constant), and $(n,m)$ chirality of SWNTs all influence their absorbivity and corresponding photoluminescence efficiency (25, 26). Our group (21), as well as others (15, 27), have indicated that the theoretically calculated absorption $[I_{\text{cal}}^\text{abs}(n,m)]$ and photoluminescence $[I_{\text{cal}}^\text{pl}(n,m)]$ intensity factors calculated by Oyama et al. (25) provide a good framework for correlating $(n,m)$ abundance between absorbance and photoluminescence results. Columns 4 and 5 of table S2 list the experimentally observed relative $(n,m)$-SWNT absorbance as obtained by absorbance and PLE results, respectively. When these results are scaled by the Oyama-derived factors (columns 7 and 8), the average divergence between the absorbance- and photoluminescence-derived abundance results (0.12) becomes less than the divergence of the unscaled abundances (0.18).

What is the nature of the significantly greater background absorption for ethylacetate and...
The profoundly intense PLE signal of toluene-dispersed FC12 dispersion, in particular that of the (6,5)-SWNTs, prompted us to determine their photoluminescence quantum yield using the method in (11). The absorbance (Fig. 4A) and emission (Fig. 4B) spectra of Styril-13 were compared with the $E_{2S}^1$ absorption and $E_{1S}^1$ emission profiles of SDS- and FC12-dispersed CoMoCAT SWNTs. The 11% quantum yield of Styril-13 at $3.3 \times 10^{-7}$ M in methanol was used as a primary reference standard because of the close excitation and emission spectral overlap with (6,5)-SWNTs (11). Before determining the quantum yield of toluene-dispersed FC12-SWNTs, we used the aqueous-dispersed SDS-SWNTs as a secondary standard (16, 17). Because the power-law background signal in both SDS and FC12 can influence significantly the nanotube quantum yield figures, we define as “sample” and “individual” quantum yield the values obtained when (6,5) absorption is taken from either zero absorbance units or the power-law fitted line, respectively. Figure S6 illustrates sample quantum yields of SDS-dispersed (6,5)-SWNTs as a function of their $E_{2S}^1$ absorption peak intensity. A value of 0.5% for the “sample” quantum yield was obtained at ultimate dilution while keeping the SDS concentration above the critical micelle concentration of ~1 weight percent (16, 17). Progressively higher concentrations decrease the quantum yield down to 0.05% and below, in accordance with (16, 17). The substantially higher photoluminescence intensity of FC12- versus SDS-dispersed SWNTs (Fig. 4B) yields a “sample” quantum yield of ~11% for (6,5)-SWNTs. When the scattering background is removed, the “individual” (6,5) quantum yield increases to ~20%.

Table 1 lists the corresponding (6,5) quantum yields for all solvents in this study. α-xylene and benzene demonstrated 17% and 10% “individual” quantum yield for (6,5)-SWNTs, respectively, with the remaining solvents showing progressively lower quantum yield values.

There may be several causes for the surprisingly large quantum yields for (6,5)-SWNTs. Near-armchair nanotubes such as (6,5)-SWNTs have been theorized to exhibit progressively higher quantum yields as their diameter decreases (25, 30), although modality and family dependence also play an important role. Such increases, however, together with recent ~8% quantum yield determination for SDS-suspended SWNTs (using single-nanotube photometry) (15), cannot explain the aforementioned 20% quantum yield value for (6,5)-SWNTs. Similarly, the possibility of selective enrichment of only (6,5)-SWNTs can equally be ruled out on the basis of one-to-one correlation between photoluminescence and NIR absorption, as well as the close resemblance of the relative photoluminescence abundance histograms for FC12- and SDS-dispersed nanotubes in fig. S2.

To pinpoint the nature of such a high quantum yield, we investigated the tight wrapping of FC12 onto nanotubes by time-dependent photoluminescence intensity traces as a function of $t_\text{irradiation}$ (9). The photoluminescence intensity of toluene FC12 dispersion remained constant (Fig. 4C). Although the reversible acid-induced p-doping of SWNTs in the presence of oxygen is well documented (7–9), less attention has been exerted on SWNT interactions with oxygen alone (8). Density functional theory calculations by Dukovic et al. (8) indicate that singlet $O_2$ chemisorbs on a (5,0)-SWNT and adopts a 1,4-endoperoxide structure (Fig. 1C). The calculated activation energy for 1,4-endoperoxide desor-
tion (~1 eV) (8) is about half of the binding energy of a single isoalloxazine moiety (~2.2 eV) (31), which suggests that chemisorbed O$_2$ should be displaced by FC12 organization around the nanotubes. As illustrated in Fig. 1C, the seamless quantum yield (1.5%) (~16) versus 0.1 to 0.5% for SDS-dispersed SWNTs (16, 17).

The origin of the large solvent variation in the observed photoluminescence quantum yield may originate in the relative solubility differences of the two FC12 submoieties (i.e., isoalloxazine ring and dodecyl side chain). We procured 10-methyl isoalloxazine (lumiflavin), the closest analog to the isoalloxazine ring, and investigated its solubility characteristics versus those of FC12. Table 1 lists the solubilities of lumiflavin and FC12 as a function of dielectric constant. The proportionality of the helix dissociation effects in the photoemission process. The highest solubility values for both lumiflavin and FC12, although SWNT photoluminescence activity is absent. Such behavior would originate from the moderate to strong H-bonding ability of pyridine and DMF, which would dissociate the H-bonded FC12 ribbon responsible for nanotube dispersion.

The “individual” quantum yield of (6,5)-SWNTs is shown in Fig. 4D as a function of FC12 solubility in each solvent (Table 1). High quantum yields (green line) were seen for low-polarity solvents, and low quantum yields (magenta line) were seen for medium-polarity solvents. For both regimes, the increase in FC12 solubility was followed by a decrease in quantum yield. Because H-bonding is responsible for both helix stability and FC12 (or lumiflavin) dissolution, increasing solvent polarity is expected to increase the helix dissociation constant and render FC12-wrapped nanotubes more prone to bundling and less able to desorb 1,4-endoperoxide defects. The proportionality of the helix dissociation constant to the FC12 solubility would account for the linear dependence of 1,4-endoperoxide defect removal along the one-dimensional SWNT structure. The uniform and defect-free environment offered by the flavin organization, which is needed as a result of the large exciton diffusion length (~90 nm) (7) in SWNTs, opens an array of new frontiers in SWNT photophysics. Moreover, the flavin organization is also compliant with the hierarchical assembly of nanotubes for device manipulation.

References and Notes
1. S. M. Bachilo et al., Science 298, 2361 (2002); published online 29 November 2002 (10.1126/science.1078727).
19. See supporting material on Science Online.

Probing the Angular Momentum Character of the Valence Orbitals of Free Sodium Nanoclusters

C. Bartels, C. Hock, J. Huwer,* R. Kuhnen, J. Schwöbel,† B. von Issendorff‡

Although many properties of polyatomic metal clusters have been rationalized by an electron shell model resembling that used for free atoms, it remained unclear how reliable this analogy is with respect to the angular momentum eigenstate character of the electronic wave functions. We studied free size-selected negatively charged clusters of sodium atoms (Na$_n^-$) of approximately spherical shape ($n = 19$, 40, 55, 58, 147) by angle-resolved photoelectron spectroscopy over a broad range of photon energies (1.5 to 5 electron volts). Highly anisotropic, state- and energy-dependent angular distributions emerged for all sizes. Well-defined classes of energy dependence related to the approximate angular momenta of the bound-state orbitals indicate that the overall character of the valence electron wave functions is not appreciably influenced by the interaction with the ion background. The measured distributions nevertheless deviate strongly from the predictions of single-electron models, hinting at a distinct role of correlated multielectron effects in the photoemission process.

Under the free-electron model, a cluster of metal atoms can be seen as a realization of the textbook case of a spherical box potential filled with a well-defined number of electrons, and therefore as an ideal model system to study the structure and dynamics of a finite-size Fermi system. In such a system, the electrons occupy angular momentum eigenstates, which leads to a highly discretized density of states—the electron shell structure ($J$, 2). By analogy with atomic orbital filling, the clusters can thus be construed as “artificial atoms” (3). Sodium is the best representative of a free-electron metal (4), and indeed it was for sodium clusters that an influence of this shell structure was initially observed (5). This result inspired a wealth of studies on simple metal clusters, and shell effects have been found in many cluster properties, for example, in the size dependences of binding energies, ionization potentials, and absorption spectra (J). Nevertheless, photoelectron spectroscopy, which in principle allows a direct imaging of

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Brightly Fluorescent Single-Walled Carbon Nanotubes via an Oxygen-Excluding Surfactant Organization

Sang-Yong Ju, William P. Kopcha, Fotios Papadimitrakopoulos*

*To whom correspondence should be addressed. E-mail: papadim@mail.ims.uconn.edu

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Materials and Methods
Figs. S1 to S6
Tables S1 and S2
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Materials and Methods:
4,5-dimethyl-1,2-phenylenediamine was purchased from TCI America. 2-[p-dimethylaminophenyl]-2,4-neopentylene-1,3,5,7-octatetraenyl]-3-ethyl-(6,7-benzo)-benzothiazolium perchlorate (Styryl-13) was obtained from Exciton. All other reagents were purchased from Sigma-Aldrich unless otherwise mentioned. All solvents used for dispersing 10-Dodecyl-7,8-dimethyl-10H-benzo[g]pteridine-2,4-dione (FC12) and FC12-dispersed single-walled carbon nanotubes (SWNTs) were reagent grade. Synthesis of FC12 was adapted according to prior literature reports,¹,² and are briefly described below. Silica gel with 230-400 mesh was used for flash chromatography. Column chromatography was performed in a Companion flash chromatography apparatus (Teledyne Isco Inc.), equipped with a single wavelength UV detector. ¹H and ¹³C NMR spectra were acquired on a Bruker DMX spectrometer operating at a Larmor frequency of 400 MHz and 100 MHz, respectively. All spectra were recorded in 5 mm NMR tubes containing 0.65 ml of CDCl₃ at 295 K. SWNT prepared by the Co/Mo catalyst (CoMoCAT, lot # SG-000-0002) was kindly donated from Southwest Nanotechnolgies Inc. Room temperature UV-Vis-NIR absorption spectra were obtained using a Perkin–Elmer LAMDA-900 UV-NIR spectrometer. Fluorescence spectroscopy measurements were conducted on a Jobin-Yvon Spex Fluorolog 3-211 spectrofluorometer equipped with a PMT near-infrared (NIR) detector. The intensities were corrected for instrumental variations in excitation intensity and detection sensitivity. 3 nm step size was utilized for both excitation and emission. Dynamic light scattering (DLS) was performed using NiCOMP 380/DLS submicron particle sizer equipped with a 633 nm laser (operating at a power of 5 mW), in which scattered light was collected at 90°. Prior to measurements, all samples were equilibrated at least for 10 min at 20°C to establish thermal and convectional stability.

![Scheme S1. Synthetic route of FC12.](image)

**Synthesis of FC12:**

N-Dodecyl-4,5-dimethyl-benzene-1,2-diamine (2): A mixture of 4.08 g (30 mmol) of 4,5-dimethyl-1,2-phenylenediamine and 2.04 g (10 mmol) of 1-chloro-dodecane in 20 mL of triethylamine was stirred at 130 °C for 6 hrs under argon. After cooling and addition of dichloromethane (100 mL), the organic solution was washed with aqueous Na₂CO₃ solution (10%, 40 mL). The aqueous layer was extracted twice with dichloromethane (MC, 2×100 mL). The combined organic extracts were dried over MgSO₄ and rotary evaporated to dryness. The thin-layer chromatography (TLC) retention factor (Rᶠ) of the target compound 2 was 0.55 with MC:methanol (MeOH) (95:5). Compound 2 was purified by flash
chromatography on silica gel in MC:MeOH (95:5) to produce 1.8 g of reddish crystals (60 % yield); mp 53-54 °C; $^1$H NMR (400 MHz, CDCl$_3$, see Figure S1) $\delta$ 6.56 (1H, s), 6.50 (1H, s), 3.20 (3H, broad s), 3.1 (2H, $J$ = 8 Hz), 2.26 (3H, s), 2.21 (3H, s), 1.68 (2H, $q$, $J$ = 7 Hz), 1.46 (2H, m), 1.34 (16H, s), 0.92 (3H, $q$, $J$ = 8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.0, 131.8, 128.1, 125.9, 118.4, 113.93, 44.7, 31.9, 29.9, 29.69, 29.65, 29.5, 29.4; Anal. Calcd. for C$_{20}$H$_{36}$N$_2$ (MW=304.51): C, 78.88; H, 11.92; N, 9.20. Found: C, 78.95; H, 12.16; N, 9.32.

10-Dodecyl-7,8-dimethyl-10$H$-benzo[g]pteridine-2,4-dione (FC12): A mixture of 0.578 g (1.9 mmol) of compound 2, 0.284 g (2 mmol) of alloxane monohydrate, 0.42 g (6 mmol) of boric oxide and 60 mL of glacial acetic acid was stirred at 60 °C for 1 hr. The resulting solution was quenched with 100 mL of water and the yellow precipitates were filtered and vacuum-dried. The $R_f$ value of FC12 by TLC was 0.85 with MC-MeOH (95:5). FC12 was purified by flash chromatography on silica gel in MC:MeOH (95:5) to produce 0.46 g of yellow crystals (58 % yield); mp 223-224 °C; $^1$H NMR (400 MHz, CDCl$_3$, see Figure S1) $\delta$ 8.85 (1H, s), 8.08 (1H, s), 7.41 (1H, s), 4.71 (2H, broad t), 2.59 (3H, s), 2.48 (3H, s), 1.88 (2H, $q$, $J$ = 8 Hz), 1.57 (2H, $q$, $J$ = 8 Hz), 1.51 (2H, m), 1.29 (14H, s), 0.90 (3H, $q$, $J$ = 8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.6, 155.2, 148.2, 137.0, 136.2, 135.0, 132.9, 131.1, 115.3, 45.36, 31.9, 29.61, 29.59, 29.54, 29.50, 29.32, 29.29, 27.16, 26.9, 22.7, 21.7, 19.5, 14.1; $\lambda_{\text{max}}$ ($\epsilon$) 443 nm (11,964 L/mol·cm in ethyl acetate); Anal. Calcd. for C$_{24}$H$_{34}$N$_4$O$_2$ (MW=410.55): C, 70.21; H, 8.35; N, 13.65; O, 7.79. Found: C, 70.09; H, 8.85; N, 13.41.

Nanotube Dispersion Protocols:

Dispersion of FC12/SWNT in organic solvents: A mixture of 1 mg of CoMoCAT-SWNT and 1 mg (2.4 μmol) of FC12 in 4 mL of organic solvents were cup-horn sonicated for 4 hrs at 300 W (Cole Parmer Ultrasonic Processor). All resulting solutions were centrifuged at 10,000 g for 20 min followed by careful collection of their supernatants, unless otherwise noted.

Dispersion of SDS/SWNT in D$_2$O: A mixture of 1 mg of CoMoCAT-SWNT and 1 wt. % of SDBS was added into 4 mL of D$_2$O, according to literature.$^3$ The solution was homogenized for 1 hr, followed by sonication for 10 min at 600W intensity. The resulting solution was centrifuged at 45,000 g for 2 hr and the supernatant (upper 80 %) was collected to produce a clear dark solution.

Dispersion of FMN/SWNT in D$_2$O: A mixture of 1 mg of CoMoCAT-SWNT and 4 mg of FMN in 4 mL of D$_2$O were cup-horn sonicated for 4 hrs at 300 W (Cole Parmer Ultrasonic Processor), as detailed elsewhere.$^4$ The solution were centrifuged at 15,000 g for 2 hrs followed by careful collection of their supernatants.
Protocols for the Deconvolution of Vis-NIR Absorption Spectra:

Background corrections for Fig. 3b&c were carried out by subtracting a power-law function \(a\lambda^{-b}\), where \(\lambda\) is the wavelength and \(a, b\) are fitted parameters, as described elsewhere.\(^5\) The \(b\) value was obtained from an optimum fit of the background signal. The optimum values of \(b\) for toluene, ethyl acetate and acetone dispersion in Fig. 3b&c were found to be 0.600, 0.815, and 0.671, respectively. Peak deconvolution using Lorentzian peak profiles were found to produce an optimum fit for the toluene sample of Fig. 3b. In the case of ethyl acetate and acetone samples, deconvolution of their NIR absorption spectra was performed using Voigt peak profiles.

Photoluminescence (PL) Quantum Yield (QY) Measurements:

PL QY was calculated using Styryl-13 (2-[p-dimethylaminophenyl]-2,4-neopentylen-1,3,5,7-octatetraenyl]-3-ethyl-(6,7-benzo)-benzothiazolium perchlorate) as a reference dye, with 11 % reported QY \((\eta_{\text{ref}})\) according to Crochet et al.\(^6\) The sample QY \((\eta_s)\) was determined based on equation (1),

\[
\eta_s = \eta_{\text{ref}} \times \frac{I_s \times \alpha_{\text{ref}} \times n_s^2}{I_{\text{ref}} \times \alpha_s \times n_{\text{ref}}^2} \tag{1}
\]

Where \(I\) is the integrated area of photoluminescence emission, \(\alpha\) is the extinction coefficient at the excitation wavelength, and \(n\) is the refractive index of the solvent, for the sample \((s)\) and reference \((\text{ref})\), respectively. The extinction coefficient \(\alpha\) was obtained from the respective peak height of the absorption band at the excitation wavelength. The concentration of all samples was adjusted to similar absorption values \((i.e.\) less than 0.05) at 580 nm. The emission spectra of Styryl-13 (in methanol), FC12/SWNTs (in toluene), and SDS/SWNTs (in D\(_2\)O) were recorded at 580, 583, and 569 nm, excitation wavelengths, using the same slit widths for the mercury lamp as well as the excitation and emission monochrometers. In order to determine the concentration dependence of PL QY of SDS-dispersed SWNTs, a stock SDS/SWNTs D\(_2\)O dispersion was diluted with 1% w/v SDS dispersion in D\(_2\)O to maintain the similar SDS concentration throughout the experiment.

Molecular Modeling:

Cerius2 simulation software was utilized for molecular modeling using the Dreiding 2.21 force field for molecular mechanics, molecular dynamics and quenched dynamics simulations, as detailed elsewhere.\(^4\) The charge equilibration method was used to set atom charges for 10-methyl isoalloxazine (lumiflavin), while zero charge was assigned for all SWNT carbon atoms. Materials Studio 4 software was used for visualization. An sp\(^3\) geometry was used for the N atom at the 10 position of the isoalloxazine ring (Scheme S1), while for the rest of the aromatic atoms an sp\(^2\) configuration was utilized. For the general approach, various helix motives \(U_t\) were constructed using symmetry operation, where \(U\) and \(t\) denote
number of helical lattice points per identical period and turns to the next identical helix point, respectively. A vertically-aligned flavin moiety was off-centered by the summated distance of half of diameter of SWNT (i.e., 0.38 nm for (6,5) nanotube) and van der Waals distance (0.34 nm). This flavin moiety was then rotated by \((360^\circ \times t)/U\) and translated by \((2.5 \text{ nm} \times t)/U\) along z-axis, which is parallel to SWNT axis. The resulting half helix was rotated along the x-axis and adjusted to generate a complementary double helix. The combined double stranded flavin helix was minimized in the periodic boundary condition, while energy-minimization to the underlying carbon nanotube was constrained. For energy-minimization of nanotube with various \(U_t\) flavin helices in periodic boundary condition, the iteration was repeated until RMS values are below 0.001 kcal/mol/atom. For the 1,4-endoperoxide defects onto SWNT (Fig. 1C), the energy-minimized configuration was found close to the reported DFT conformation. A purple shading was added to the 1,4-endoperoxide of Fig. 1C to better visualize the radii of space-filled oxygen atoms.
**Figure S1.** $^1$H NMR spectra of compound 2 and FC12. Green and black stars indicate peaks from CDCl$_3$ and residual water.

**Compound 2 (400MHz, CDCl$_3$)**

![NMR spectrum of Compound 2](image)

**Compound 3 (400MHz, CDCl$_3$)**

![NMR spectrum of Compound 3](image)

**Figure S2.** Relative PL intensity of FC12/SWNTs in various solvents, plotted as a function of nanotube diameter. Relative PL intensity of SDS/SWNTs was also presented. All peak intensities are listed in Table S2 and the total sum is 100%.

![Relative PL intensity](image)
Figure S3. Excitation slices at 1047 nm emission from Fig. 2a-d.

Figure S4. Absorption spectra close-up from ethyl acetate (a) and acetone (b), along with their deconvoluted components in the absence of the orange-colored Gaussian peak contribution shown in Fig. 3c (top two spectra). Red curve shows the summated absorption spectra from the color-coded individual fitting curves, while circled curves depict the background subtracted, experimentally obtained absorption spectra.
**Figure S5.** Auto-correlation function ($C(t)$) of dynamic light scattering (DLS) of FC12/SWNTs dispersed in toluene (black) and ethylacetate (red).

![Figure S5](image)

**Figure S6.** (6,5)-SWNT “sample” photoluminescence (PL) quantum yields (QYs) for SDS-dispersed nanotubes in D$_2$O as a function of its $E_{22}^{S}$ absorption peak intensity. Inset illustrates the SDS-dispersed (6,5)-SWNT PL peak area change as a function of its $E_{22}^{S}$ absorption peak intensity.

![Figure S6](image)
Table S1. PLE-derived $E^S_{11}$ and $E^S_{22}$ positions and relative PL intensities from Figure 2a-d.

<table>
<thead>
<tr>
<th>Nanotube Assignment</th>
<th>Diameter $d_i$</th>
<th>Chiral Angle $\theta$</th>
<th>Benzene $E^S_{11}$, $E^S_{22}$, FWHM, Rel. Int.</th>
<th>Toluene $E^S_{11}$, $E^S_{22}$, FWHM, Rel. Int.</th>
<th>Ethyl acetate $E^S_{11}$, $E^S_{22}$, FWHM, Rel. Int.</th>
<th>Acetone $E^S_{11}$, $E^S_{22}$, FWHM, Rel. Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9,1)</td>
<td>0.757</td>
<td>5.21</td>
<td>945.1, 707.0, 24.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6,5)</td>
<td>0.757</td>
<td>27.00</td>
<td>993.8, 582.8, 33.70, 1.000</td>
<td>998.7, 582.4, 39.31, 1.000</td>
<td>998.8, 582.5, 41.50, 1.000</td>
<td></td>
</tr>
<tr>
<td>(8,3)</td>
<td>0.782</td>
<td>15.30</td>
<td>982.0, 674.8, 20.70, 0.236</td>
<td>987.8, 674.0, 34.28, 0.381</td>
<td>989.3, 674.2, 31.36, 0.352</td>
<td></td>
</tr>
<tr>
<td>(7,5)</td>
<td>0.829</td>
<td>24.50</td>
<td>1048.6, 655.9, 29.58, 0.411</td>
<td>1056.4, 654.7, 35.87, 0.363</td>
<td>1052.7, 658.9, 55.13, 0.296</td>
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<tr>
<td>(8,4)</td>
<td>0.840</td>
<td>19.11</td>
<td>1125.7, 603.2, 29.00, 0.173</td>
<td>1139.8, 606.9, 42.07, 0.205</td>
<td>1143.9, 607.9, 51.38, 0.176</td>
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<tr>
<td>(7,6)</td>
<td>0.895</td>
<td>27.46</td>
<td>1152.2, 659.5, 30.70, 0.165</td>
<td>1147.2, 658.9, 42.51, 0.193</td>
<td>1154.3, 659.1, 51.34, 0.184</td>
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<tr>
<td>(9,4)</td>
<td>0.916</td>
<td>17.48</td>
<td>1122.5, 740.1, 29.00, 0.081</td>
<td>1131.1, 735.3, 44.35, 0.126</td>
<td>1136.0, 741.3, 51.80, 0.118</td>
<td></td>
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<tr>
<td>(8,6)</td>
<td>0.966</td>
<td>25.28</td>
<td>1204.6, 737.8, 23.23, 0.091</td>
<td>1207.9, 736.2, 30.16, 0.139</td>
<td>1216.8, 735.3, 37.48, 0.167</td>
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<tr>
<td>(9,5)</td>
<td>0.976</td>
<td>20.63</td>
<td>1272.2, 691.6, 24.05, 0.094</td>
<td>1275.8, 687.8, 38.36, 0.081</td>
<td>1279.2, 688.0, 39.79, 0.092</td>
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<tr>
<td>(8,7)</td>
<td>1.032</td>
<td>27.80</td>
<td>1308.0, 744.1, 22.91, 0.075</td>
<td>1308.0, 744.1, 22.91, 0.049</td>
<td>1308.5, 743.0, 47.36, 0.099</td>
<td></td>
</tr>
</tbody>
</table>
Table S2. \((n,m)\) abundance evaluation of FC12/SWNTs in toluene as determined from their Vis-NIR absorption (Fig. 3b) and PLE map (Fig. 2b and Table S1), listed for increasing nanotube diameter \((d_t)\).

<table>
<thead>
<tr>
<th>Assign. ((n,m))</th>
<th>(d_t) (nm)</th>
<th>FWHM (meV)</th>
<th>(\text{Abs}_{\text{measured}}) (%)</th>
<th>(\text{PL}_{\text{measured}}) Intensity (%)</th>
<th>Divergence(^\text{¥})</th>
<th>Abs. scaling factor(^\text{§})</th>
<th>PL scaling factor(^\text{§})</th>
<th>Scaled Abs (%)</th>
<th>Scaled PL (%)</th>
<th>Divergence(^\text{¥})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((9,1))</td>
<td>0.76</td>
<td>15.8</td>
<td>1.8</td>
<td>0.5</td>
<td>0.28</td>
<td>2.75</td>
<td>0.70</td>
<td>1.3</td>
<td>0.4</td>
<td>0.26</td>
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<tr>
<td>((6,5))</td>
<td>0.76</td>
<td>24.6</td>
<td>50.1</td>
<td>42.4</td>
<td>0.04</td>
<td>1.85</td>
<td>0.67</td>
<td>52.7</td>
<td>40.4</td>
<td>0.07</td>
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<tr>
<td>((8,3))</td>
<td>0.78</td>
<td>15.1</td>
<td>4.2</td>
<td>11.0</td>
<td>0.22</td>
<td>2.43</td>
<td>2.13</td>
<td>3.3</td>
<td>3.3</td>
<td>0.00</td>
</tr>
<tr>
<td>((7,5))</td>
<td>0.83</td>
<td>18.7</td>
<td>8.6</td>
<td>18.7</td>
<td>0.18</td>
<td>2.04</td>
<td>0.71</td>
<td>8.2</td>
<td>16.8</td>
<td>0.17</td>
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<tr>
<td>((8,4))</td>
<td>0.84</td>
<td>19.4</td>
<td>3.8</td>
<td>8.2</td>
<td>0.18</td>
<td>1.77</td>
<td>0.46</td>
<td>4.2</td>
<td>11.4</td>
<td>0.23</td>
</tr>
<tr>
<td>((7,6))</td>
<td>0.90</td>
<td>30</td>
<td>11.3</td>
<td>6.2</td>
<td>0.15</td>
<td>1.98</td>
<td>0.47</td>
<td>11.1</td>
<td>8.4</td>
<td>0.07</td>
</tr>
<tr>
<td>((9,4))</td>
<td>0.92</td>
<td>12.1</td>
<td>1.2</td>
<td>3.8</td>
<td>0.26</td>
<td>2.27</td>
<td>0.70</td>
<td>1.1</td>
<td>3.5</td>
<td>0.26</td>
</tr>
<tr>
<td>((8,6))</td>
<td>0.97</td>
<td>16.8</td>
<td>5.5</td>
<td>4.6</td>
<td>0.04</td>
<td>2.18</td>
<td>0.49</td>
<td>4.9</td>
<td>6.0</td>
<td>0.05</td>
</tr>
<tr>
<td>((9,5))</td>
<td>0.98</td>
<td>18.6</td>
<td>6.0</td>
<td>2.2</td>
<td>0.23</td>
<td>1.88</td>
<td>0.28</td>
<td>6.3</td>
<td>5.1</td>
<td>0.05</td>
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<tr>
<td>((8,7))</td>
<td>1.03</td>
<td>21.7</td>
<td>7.4</td>
<td>2.4</td>
<td>0.26</td>
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<td>0.30</td>
<td>7.0</td>
<td>5.2</td>
<td>0.07</td>
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</table>

\(^{\text{¥}}\) Divergence: \(0.5\times|\%\text{Abs} - \%\text{PL}|/(\%\text{Abs} + \%\text{PL})\)
\(^{\text{§}}\) according to Oyama et al.\(^8\)

Cited References