Carbon nanotubes as photoprotectors of organic dyes: reversible photoreaction instead of permanent photo-oxidation

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UV-vis absorption spectra

Figure S1. Absorption spectra of RhB (black line) and RhB/SWNT (red line) in aqueous solutions.

Determination the fluorescence quantum yield of RhB/SWNT in solution

In order to estimate the fluorescence quantum yield of RhB molecules after they are attached to the surfaces of SWNTs in aqueous solution, we measured fluorescence intensity of RhB and RhB/SWNT solutions having the same concentration of the dye (RhB, $3 \times 10^{-7}$ mol L$^{-1}$) under the same experimental conditions (excitation at 530 nm). An excess amount of SWNTs was used to make sure that a majority of RhB molecules were adsorbed onto the surfaces of the nanotubes. The fluorescence intensity was calibrated to remove the inner-filter effect caused by the absorption of SWNTs at the RhB emission range. By comparing the fluorescence intensity of RhB/SWNT solution to that of RhB solution, we estimated the ratio of the fluorescence quantum yields $\Phi_{\text{RhB/SWNT}} / \Phi_{\text{RhB}}$ to be 0.17. This value is in consistence with that obtained from the microscopy measurements described in the main text. Moreover, it agrees well with the fluorescence quenching efficiency of RhB by addition of SWNT reported previously. For HiPco
SWNT, the maximum quenching efficiency is reported to be 84.3%, which is the same as obtained by us (1 - 0.17 = 0.83).

**Deducing of the expression for the recovery coefficient (R)**

We used a simple reaction scheme to describe the reversible process between the emissive and dark states of RhB molecules in the nanohybrids:

\[
\begin{align*}
\text{"Bleaching":} & \quad F + h\nu \xrightarrow{k_1} D \quad (S1a) \\
\text{Recovery:} & \quad D \xrightarrow{k_2} F \quad (S1b)
\end{align*}
\]

where \(k_1\) and \(k_2\) are the rate constants of the corresponding processes.

We assume that RhBs in their emissive state (F) have a certain fluorescence quantum yield (constant) while in the dark state D the fluorescence quantum yield is equal to zero. Therefore, the fluorescence intensity is directly proportional to the population of the emissive state F.
Figure S2. Transient bleaching and recovery trace for an individual RhB/SWNT nanohybrid under interrupted CW laser excitation calculated in the framework of the reaction scheme (S1). I₀, I₁, I₂,…, Iₙ marked here is the fluorescence intensity of each step, respectively. t₀, tₕ₃₅₁, …  tₜ₃₅ₙ is the time that the sample was illuminated by laser or kept in dark, respectively.

Using the parameters introduced at the Figure S2 and the reaction (S1a) and (S1b), the first bleaching step during the time t₀ (laser is on) is:

\[ I₁ = I₀ - \exp\left[-\left(k₁ - k₂\right)t₀\right] \]  \hspace{1cm} (S2)

where t₀ is the time that the laser illuminates the sample during the first bleaching period.

After the first dark period (tₜ₃₅₁), the recovery coefficient R₁ is defined as (the main text Equation (2)):

\[ R₁ = \frac{I₂ - I₁}{I₀ - I₁} \]  \hspace{1cm} (S3)

I₂ is the fluorescence intensity just upon the laser being turned on after the dark period. It is larger than I₁ because the recovery reaction (S1b) is proceeding in darkness, which causes repopulation of RhB to the emissive state. I₂ can be expressed as:

\[ I₂ = I₁ + (I₀ - I₁)\left[1 - \exp\left(-k₂tₜ₃₅₁\right)\right] \]  \hspace{1cm} (S4)

The first part (I₁) of the Equation (S4) represents the residual population of RhB at the end of the bleaching first step, while the second part, \((I₀ - I₁)\left[1 - \exp\left(-k₂tₜ₃₅₁\right)\right]\), is the portion of RhB molecules recovered during the tₜ₃₅₁ period.

By substituting Equation (S4) into Equation (S3), we obtain:

\[ R₁ = \frac{I₁ + (I₀ - I₁)\left[1 - \exp\left(-k₂tₜ₃₅₁\right)\right] - I₁}{I₀ - I₁} = 1 - \exp\left(-k₂tₜ₃₅₁\right) \]  \hspace{1cm} (S5)

The recovery coefficient R₂ after the second dark period (tₜ₃₅₂) can be calculated in the same way:

\[ R₂ = \frac{I₄ - I₃}{I₀ - I₃} = \frac{I₃ + (I₀ - I₃)\left[1 - \exp\left(-k₂tₜ₃₅₂\right)\right] - I₃}{I₀ - I₃} = 1 - \exp\left(-k₂tₜ₃₅₂\right) \]  \hspace{1cm} (S6)
From Equation (S5) and (S6), one can see that the recovery coefficient does not depend on pre-history of the illumination but depends only on the time the object was kept in darkness in the last period. Of course this is true only if the reaction scheme S1 is valid.

So, $R_n$ for the $n^{th}$ step after a given time in darkness ($t_{\text{dark},n}$) is:

$$R_n = 1 - \exp(-k_2 t_{\text{dark},n})$$

(S7)

**Difference in blinking/bleaching behaviors between single RhB molecules placed on bare glass or adsorbed to SWNT surfaces**

![Figure S3](image-url)  

**Figure S3.** Typical fluorescence traces of single RhB molecule on glass substrate (top row) and single RhB molecule adsorbed to SWNT (bottom row).

**Determination the number of RhB on adsorbed to SWNT**

We used the strategy reported previously\(^2\) to determine the number of RhB on an individual SWNT. The idea is that under the same experimental condition the total fluorescence intensity of
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an ensemble of molecules is the sum of the fluorescence intensities of every individual molecule in the ensemble. The detected fluorescence emission rate $F(t)$ is defined as:

$$F(t) = \eta \frac{\sigma \Phi(t, I) I}{\nu}$$  \hspace{1cm} (S8)

where $\eta$ is the combined efficiency of photon collection and detection, $\Phi(t, I)$ is the fluorescence quantum yield, $\sigma$ is the absorption cross section at the excitation frequency $\nu$, $I$ is the excitation power density.

In order to exclude the possible excitation power fluctuations, we used a parameter called fluorescence brightness, $B$, which is independent on the excitation power density. It can be obtained from $F(t)$ by dividing by the excitation power density $I$, and it can be experimentally measured as well:

$$B(t) = \frac{F(t)}{I} = \eta \frac{\sigma \Phi(t, I)}{\nu}$$  \hspace{1cm} (S9)

Therefore, comparing the determined fluorescence brightness for the entire RhB/SWNT nanohybrid ($B_0$) to that of single molecule of RhB attached to SWNT ($B_{\text{single}}$):

$$\frac{B_0}{B_{\text{single}}} = \frac{\frac{\eta_0 \sigma_0 \Phi_0(t, I)}{\nu}}{\eta_{\text{single}} \sigma_{\text{single}} \Phi_{\text{single}}(t, I)} = \frac{\sigma_0 \Phi_0(t, I)}{\sigma_{\text{single}} \Phi_{\text{single}}(t, I)}$$  \hspace{1cm} (S10)

where $\sigma_0 \Phi_0(t, I)$ is the collective fluorescence for an individual RhB/SWNT nanohybrids containing a certain number ($N_{\text{RhB}}$) of dye molecules. As above-mentioned, the collective fluorescence intensity of RhB/SWNT is the sum of individual dye molecules attached to the SWNT surface. It can be expressed as:

$$\sigma_0 \Phi_0(t, I) = N_{\text{RhB}} \sigma_{\text{single}} \Phi_{\text{single}}(t, I)$$  \hspace{1cm} (S11)

Therefore:

$$N_{\text{RhB}} = \frac{B_0}{B_{\text{single}}}$$  \hspace{1cm} (S12)

This is the Equation (5) listed in the main text.
Using Equation (S12), one can measure the number of RhB molecules in a given RhB/SWNT nanohybrid only by collecting the fluorescence intensity from the recorded images and using the single molecule of RhB as the control sample.

In our case, the determined brightness of single RhB molecule on SWNT ($B_{\text{single}}$) is 9 collected photons s$^{-1}$ W$^{-1}$ cm$^2$ (average value for over 530 molecules attached on SWNT).

References
