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

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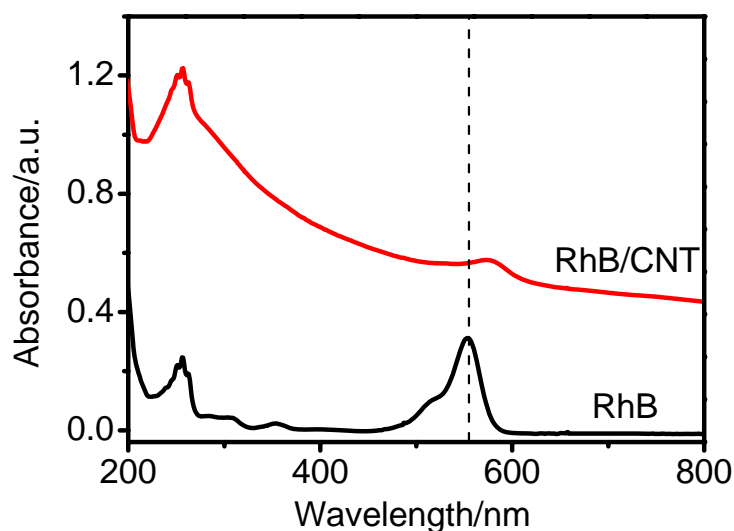
UV-vis absorption spectra

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, 3×10^{-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 $\Phi_{RhB/SWNT}$/ Φ_{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.[1] 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:

"Bleaching": $\quad F + h\nu \xrightarrow{k_1} D$ $\qquad$ (S1a)

Recovery: $\quad D \xrightarrow{k_2} F$ $\qquad$ (S1b)

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.
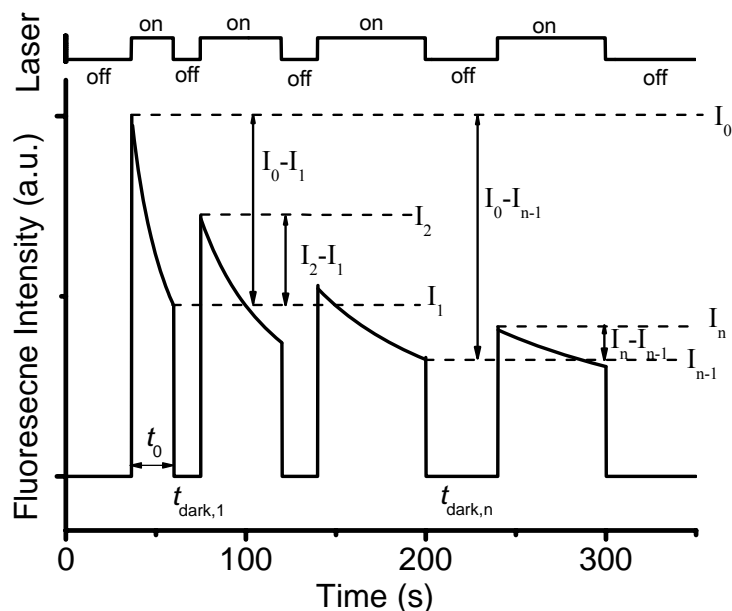
Figure S2. Transient bleaching and recovery trace for an individual RhB/SWNT nanohybrid under interrupted CW laser excitation calculated in the framework of the reaction scheme (S1). I_0, I_1, I_2,…, I_n marked here is the fluorescence intensity of each step, respectively. t_0, $t_{dark,1}$, … $t_{dark,n}$ 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 t_0 (laser is on) is:

$$I_1 = I_0 - \exp[-(k_1 - k_2)t_0] \tag{S2}$$

where t_0 is the time that the laser illuminates the sample during the first bleaching period.

After the first dark period ($t_{dark,1}$), the recovery coefficient R_1 is defined as (the main text Equation (2)):

$$R_1 = (I_2 - I_1)/(I_0 - I_1) \tag{S3}$$

I_2 is the fluorescence intensity just upon the laser being turned on after the dark period. It is larger than I_1 because the recovery reaction (S1b) is proceeding in darkness, which causes repopulation of RhB to the emissive state. I_2 can be expressed as:

$$I_2 = I_1 + (I_0 - I_1)[1 - \exp(-k_2 t_{dark,1})] \tag{S4}$$

The first part (I_1) of the Equation (S4) represents the residual population of RhB at the end of the bleaching first step, while the second part, $(I_0 - I_1)[1 - \exp(-k_2 t_{dark,1})]$, is the portion of RhB molecules recovered during the $t_{dark,1}$ period.

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

$$R_1 = \{I_1 + (I_0 - I_1)[1 - \exp(-k_2 t_{dark,1})] - I_1\}/(I_0 - I_1) = 1 - \exp(-k_2 t_{dark,1}) \tag{S5}$$

The recovery coefficient R_2 after the second dark period ($t_{dark,2}$) can be calculated in the same way:

$$R_2 = (I_4 - I_3)/(I_0 - I_3)$$

$$= \{I_3 + (I_0 - I_3)[1 - \exp(-k_2 t_{dark,2})] - I_3\}/(I_0 - I_3)$$

$$= 1 - \exp(-k_2 t_{dark,2}) \tag{S6}$$

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 nth step after a given time in darkness ($t_{dark,n}$) is:

$$R_n = 1 - \exp(-k_2 t_{dark,n}) \tag{S7}$$

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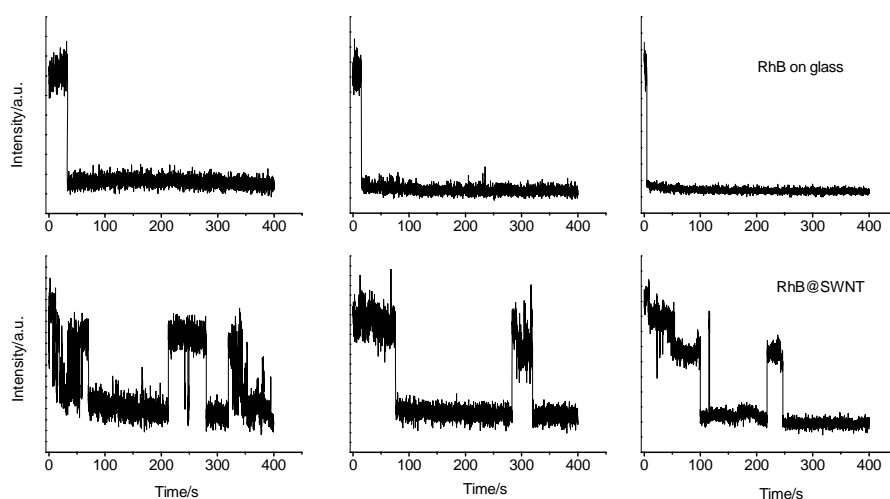

Figure S3. Typical fluorescence traces of single RhB molecule on glass substrate (top row) and single RhB molecule adsorbed to SWNT (bottom row).

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

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:

$$F(t) = \eta \frac{\sigma \Phi(t,I)I}{h\nu} \tag{S8}$$

where η is the combined efficiency of photon collection and detection, $\Phi(t, I)$ is the fluorescence quantum yield, σ is the absorption cross section at the excitation frequency ν, 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:

$$B(t) = \frac{F(t)}{I} = \eta \frac{\sigma \Phi(t,I)}{h\nu} \tag{S9}$$

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_{single}):

$$\frac{B_0}{B_{single}} = \frac{\dfrac{\eta_0 \sigma_0 \Phi_0(t,I)}{h\nu}}{\dfrac{\eta_{single} \sigma_{single} \Phi_{single}(t,I)}{h\nu}} = \frac{\sigma_0 \Phi_0(t,I)}{\sigma_{single} \Phi_{single}(t,I)} \tag{S10}$$

where $\sigma_0 \Phi_0(t,I)$ is the collective fluorescence for an individual RhB/SWNT nanohybrids containing a certain number (N_{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:

$$\sigma_0 \Phi_0(t,I) = N_{RhB} \sigma_{single} \Phi_{single}(t,I) \tag{S11}$$

Therefore:

$$N_{RhB} = \frac{B_0}{B_{single}} \tag{S12}$$

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_{single}) is 9 collected photons s^{-1} W^{-1} cm^2 (average value for over 530 molecules attached on SWNT).

References

1   A. Ahmad, T. Kurkina, K. Kern and K. Balasubramanian, *Chemphyschem* 2009, **10**, 2251-2255.

2   H. Z. Lin, R. Camacho, Y. X. Tian, T. E. Kaiser, F. Wurthner and I. G. Scheblykin, *Nano Lett.* 2010, **10**, 620-626.