Facile Method to Prepare pH-Sensitive PEI-Functionalized Carbon Nanotubes As Rationally Designed Vehicles For NSAIDs Delivery

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Supplementary Information

FIGURES

S1. IR spectra

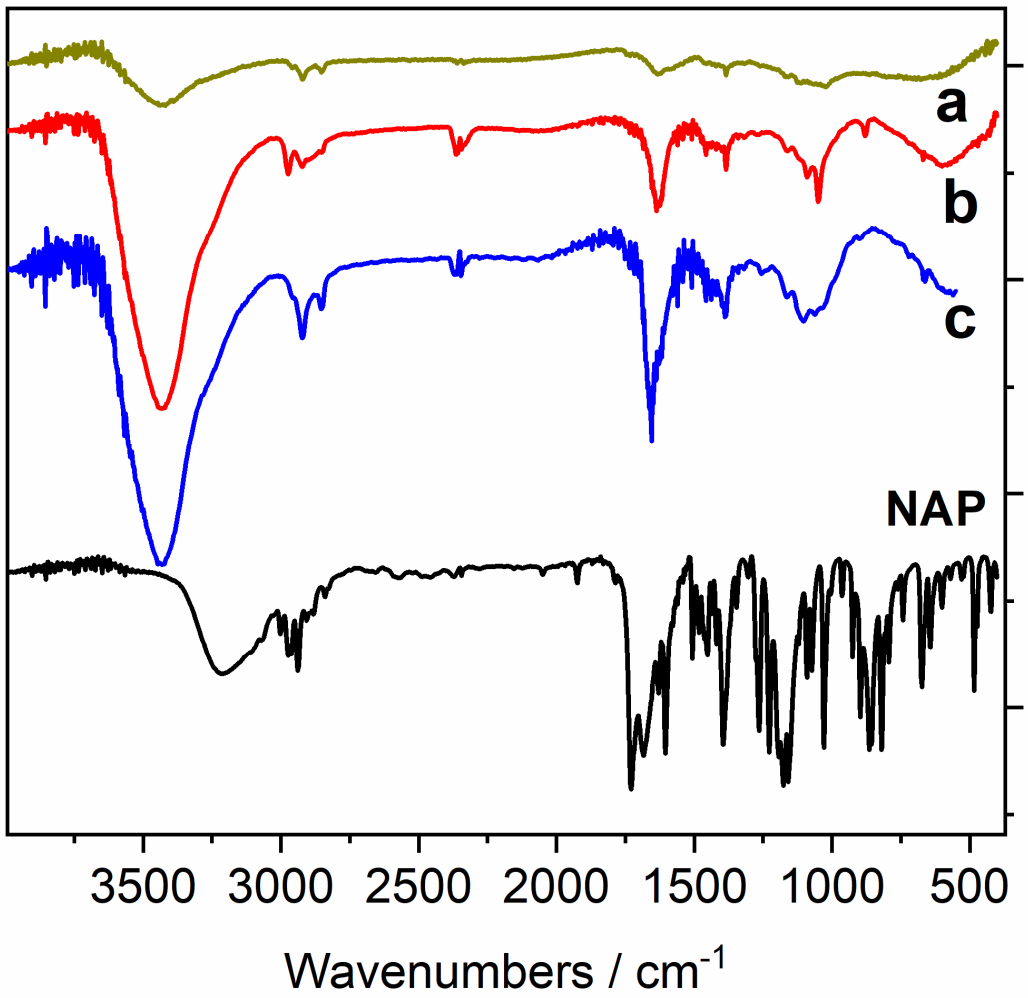

Figure S1. IR spectra of the a) carboxylated MWCNTs (NL002) b) The PEI-functionalized MWCNTS (NL003) and c) the final hybrid material MWCNTS@PEI@NAP (NL004); and the NAP (NAPROXEN) drug.

S2. Interaction with serum albumins

The extent of the inner-filter effect can be roughly estimated with the following formula:

$$I_{corr} = I_{meas} \times 10^{\frac{\varepsilon(\lambda_{exc})cd}{2}} \times 10^{\frac{\varepsilon(\lambda_{em})cd}{2}} \quad \text{(eq. S1)}$$

where I_{corr} = corrected intensity, I_{meas} = the measured intensity, c = the concentration of the quencher (i.e. compound under study), d = the cuvette (1 cm), $\varepsilon(\lambda_{exc})$ and $\varepsilon(\lambda_{em})$ = the ε of the quencher at the excitation and the emission wavelength, respectively, as calculated from the UV-vis spectra of the quencher [1].

The Stern-Volmer and Scatchard graphs are used in order to study the interaction of a quencher with serum albumins. According to Stern-Volmer quenching equation [2]:

$$\frac{Io}{I} = 1 + k_q \tau_0 [Q] = 1 + K_{SV}[Q] \quad \text{(eq. S2)}$$

where Io = the initial tryptophan fluorescence intensity of SA, I = the tryptophan fluorescence intensity of SA after the addition of the quencher (i.e. compound under study), k_q = the quenching constant, K_{SV} = the Stern-Volmer constant, τ_o = the average lifetime of SA without the quencher, [Q] = the concentration of the quencher. K_{SV} (M^{-1}) is obtained by the slope of the diagram Io/I *versus* [Q], and the quenching constant (k_q, $M^{-1}s^{-1}$) is calculated from eq. S3, with $\tau_o = 10^{-8}$ s as fluorescence lifetime of tryptophan in SA:

$$K_{SV} = k_q \tau_o \quad \text{(eq. S3)}$$

From the Scatchard equation [3]:

$$\frac{\Delta I / Io}{[Q]} = nK - K\frac{\Delta I}{Io} \quad \text{(eq. S4)}$$

where n is the number of binding sites per albumin and K is the SA-binding constant, K (in M^{-1}) is calculated from the slope in plot (ΔI/Io)/[Q] *versus* ΔI/Io and n is given by the ratio of y intercept to the slope [3].

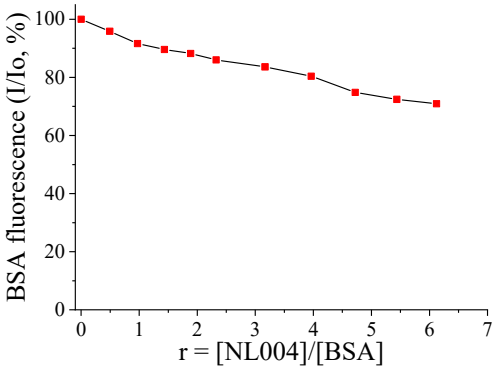

Figure S2. Plot of relative BSA fluorescence emission intensity at λ_{em} = 343 nm (I/Io, %) *versus* r (r = [NL004]/[BSA]) (up to 70.9% of the initial BSA fluorescence) in buffer solution (150 mM NaCl and 15 mM trisodium citrate at pH 7.0) in the presence of NL004.

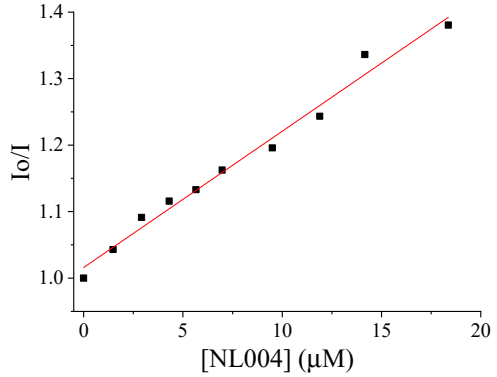

Figure S3. Stern-Volmer quenching plot of BSA for NL004.

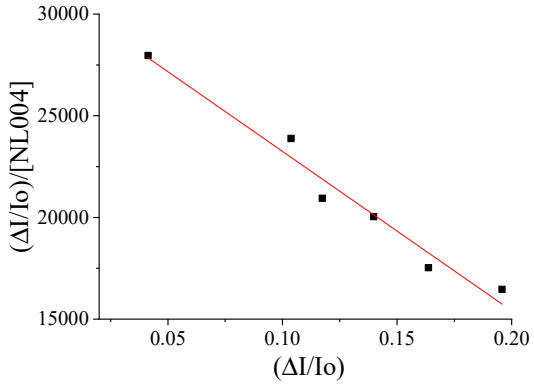

Figure S4. Scatchard plot of BSA for NL004.

S3. Interaction with CT DNA

The DNA-binding constant (K_b in M^{-1}) can be obtained by monitoring the changes in the absorbance at the corresponding λ_{max} with increasing concentrations of CT DNA and it is given by the ratio of slope to the y intercept in plots [DNA]/(ε_A-ε_f) *versus* [DNA], according to the Wolfe-Shimer equation [4]:

$$\frac{[DNA]}{(\varepsilon_A - \varepsilon_f)} = \frac{[DNA]}{(\varepsilon_b - \varepsilon_f)} + \frac{1}{K_b(\varepsilon_b - \varepsilon_f)} \qquad \text{(eq. S5)}$$

where [DNA] is the concentration of DNA in base pairs, $\varepsilon_A = A_{obsd}/[NL004]$, ε_f = the extinction coefficient for the free compound and ε_b = the extinction coefficient for the compound in the fully bound form.

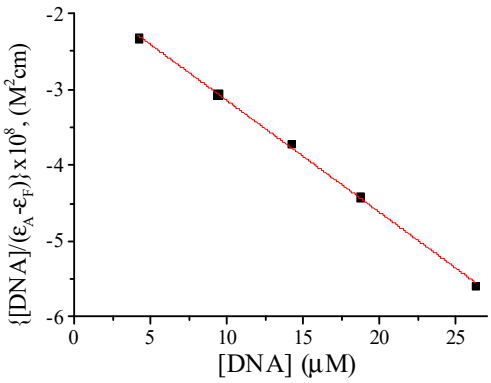

Figure S5. Plot of [DNA]/(ε_A-ε_f) *versus* [DNA] for NL004.

S4. Competitive studies with EB

The Stern-Volmer constant (K_{SV}, in M^{-1}) is used to evaluate the quenching efficiency for the compound under study according to the Stern-Volmer equation (eq. S2) [2], where Io and I are the emission intensities of the EB-DNA solution in the absence and the presence of the quencher, respectively, [Q] is the concentration of the quencher (i.e. compound under study), τ_o = the average lifetime of the emitting system without the quencher and k_q = the quenching constant. K_{SV} is obtained from the Stern-Volmer plot by the slope of the diagram Io/I *versus* [Q]. Taking τ_o = 23 ns as the fluorescence lifetime of the EB-DNA system [5], the quenching constants (k_q, in $M^{-1}s^{-1}$) of the compound can be determined according to eq. S3.

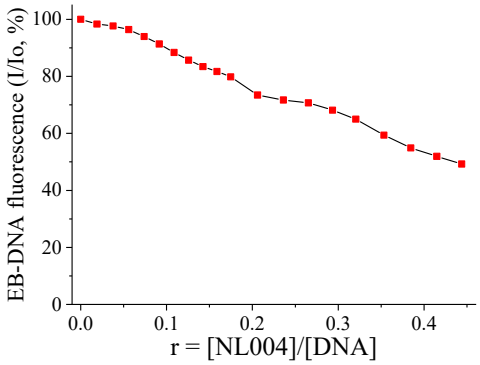

Figure S6. Plot of relative EB-DNA fluorescence emission intensity (I/Io, %) at λ_{em} = 592 nm *versus* r (r = [NL004]/[DNA]) in buffer solution (150 mM NaCl and 15 mM trisodium citrate at pH 7.0) in the presence of NL004.

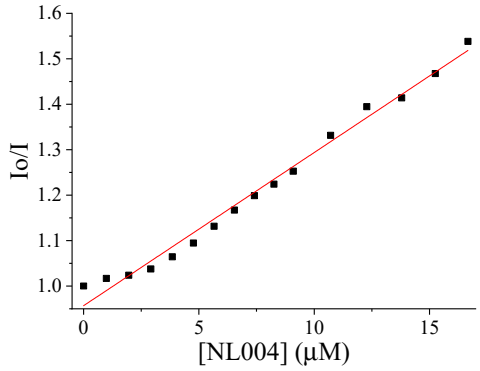

Figure S7. Stern-Volmer quenching plot of EB-DNA fluorescence for NL004.

S5. References

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