Electronic Supplementary Information (ESI)

Environmentally sensitive nanohydrogels decorated with three-strand oligonucleotide helix for controlled loading and prolonged release of intercalators

Wioletta Liwinska, Michał Symonowicz, Iwona Stanislawskab, Marek Lypb, Zbigniew Stojekac, Ewelina Zabostad,*

ac Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland
bd College of Rehabilitation, Kasprzaka 49, Warsaw, Poland

d*ezabost@chem.uw.edu.pl

Formulas used in Electrochemical Impedance Spectroscopy (EIS) analysis

The impedance of the CPE parameter in the Ershler – Randles model applied in fitting calculated data to experimental EIS points is described by Eq.(1):

\[ Z_{CPE} = T^{-1} (j \omega)^{-\phi} \]  

(1)

where, \( \omega \) is angular frequency, \( j = (-1)^{1/2} \), \( T \) is capacitive coefficient, and \( \phi \) is the exponent value.

The average double layer capacitance, \( C_{dl} \) is combined with the capacitive coefficient \( T \) and can be calculated according to Eq. (2):

\[ T = C_{dl}^{\phi} (R_s^{-1} R_{CT}^{-1})^{1-\phi} \]  

(2)

where \( R_s \) and \( R_{CT} \) are the values of solution resistance and the resistance of the charge transfer.

As the semi-infinitive diffusion of 1-electron simple redox species ([Fe(CN)_6]^{3-/4-}) takes place, the mass transfer resistance (Warburg impedance, \( W \)), visible in EIS plots as a linear part (see Fig.5 of ms.), can be estimated from Eq.(3):
\[ W = \sigma \alpha^{1/2} (1 - j) \]  

where the Wartburg parameter, \( \sigma \), is described as (Eq.(4)):

\[ \sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left( \frac{1}{D_o C_o} + \frac{1}{\sqrt{D_R C_R}} \right) \]  

and \( D_o \) and \( C_o \) are diffusion coefficient and concentration of oxidized form, respectively, and \( D_R \) and \( C_R \) are diffusion coefficient and concentration of the reduced form of the redox species.

The electron transfer-rate constant, \( k_0 \), can be determined using Eq. (5):

\[ k_0 = \left( \frac{\sigma}{R_{CT}} \right) \frac{2\xi \alpha}{2D_{ox}} \]  

where \( k_0 \) is electron-transfer rate constant, \( \xi = \sqrt{D_{ox}/D_{Red}} \) (for 1-electron, fast and reversible electrode process of \([\text{Fe(CN)}_6]^{3/-4} \approx 1 \)), \( \alpha \) is transfer coefficient and is assumed to be equal to 0.5, \( D_{ox} \) is the diffusion coefficient of \([\text{Fe(CN)}_6]^{3/-4} \) that was taken from \(^{1}\) as 0.896 \( \times 10^{-5} \text{ cm}^2\text{s}^{-1} \) and corrected to the value of 0.726 \( \times 10^{-5} \text{ cm}^2\text{s}^{-1} \), as the diffusion coefficient of \([\text{Fe(CN)}_6]^{3/-4} \) has 19% lower values in the PNIPA gel environment compared to aqueous conditions \(^{2}\).
1. Figures

- Oligo 1 5’ Acryd-GGGGG-GCTTTGGAAC 3’
- Oligo 2 5’ Acryd GGGGG-TGAGTAGACACT 3’

**Fig. 1S** Simulation of the ability of oligo1 and oligo2 strands for additional selfhybridization.
- Oligo 1-2 5’ Acryd GGGGG-TGAGTAGACACTGCTCTGGAAC-TGGGGG Acryd-3’
- Oligo 3 3’ ACTCATCTGTGACGAGACCTTGA 5’

Fig. 2S Simulation of the ability of oligo1-2 and oligo3 strands for selfhybridization.
Fig. 3S Simulation of the $T_m$ and $C_p$ of oligo1-2-3 tri-segment hybrid.
Fig. 4S Sizes of PNIPA-co-AAc (A), PNIPA-co-AAc-oligo1-2 (B) and PNIPA-AAc-oligo1-2-3 nanogels (C) obtained by DLS at 37 and 45 °C, respectively.
Fig. 5S Zeta potentials of PNIPA-co-AAc- (A), PNIPA-co-AAc-oligo1-2- (B) and PNIPA-AAc-oligo1-2-3 nanogels (C) recorded by DLS at 37 and 45°C, respectively.
Fig. 6S Plots of log (Mf/Mt) vs. log t constructed according to Peppas model in selected ranges of time (A-D) for the release of doxorubicin from: PNIPA-co-AAc- (black circles), PNIPA-co-AAc-oligo1-2- (red triangles) and PNIPA-AAc-oligo1-2-3 nanogels (blue squares). Temperature: 37 °C (filled symbols), 45°C (empty symbols).