Electron Transfer Through H-bonded Peptide Assemblies

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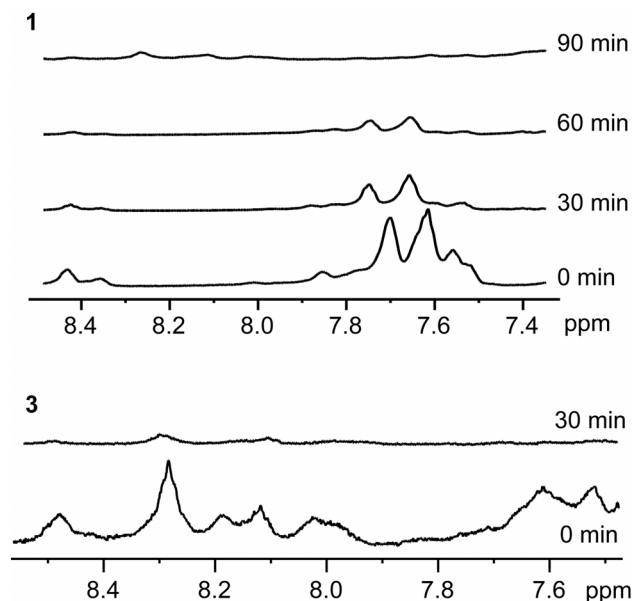
Supporting Information

Figure 1. Expanded portion of the Amide A region showing exchange of N-H signal due to for Fc-peptide conjugates **1** and **3**. A drop of D_2O was added to $CDCl_3$ solutions of **1** and **3**. For **1**, the H/D exchanged occurred at room temperature over a 90 minute period. Whereas, peptides **2** and **3** required heating of the sample at 58 °C for 30 minutes to obtain complete H/D exchange.
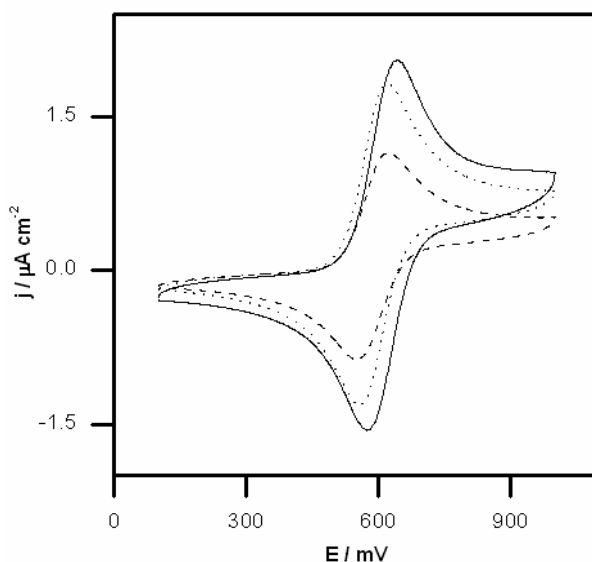

Figure 2. Solution electrochemistry of Fc-Peptides **1 - 3** in 0.1 M TBAP/CH_3CN at a Scan rate of 100 mV·s^{-1} **1** ( ), **2** ( ), **3**( )**.**
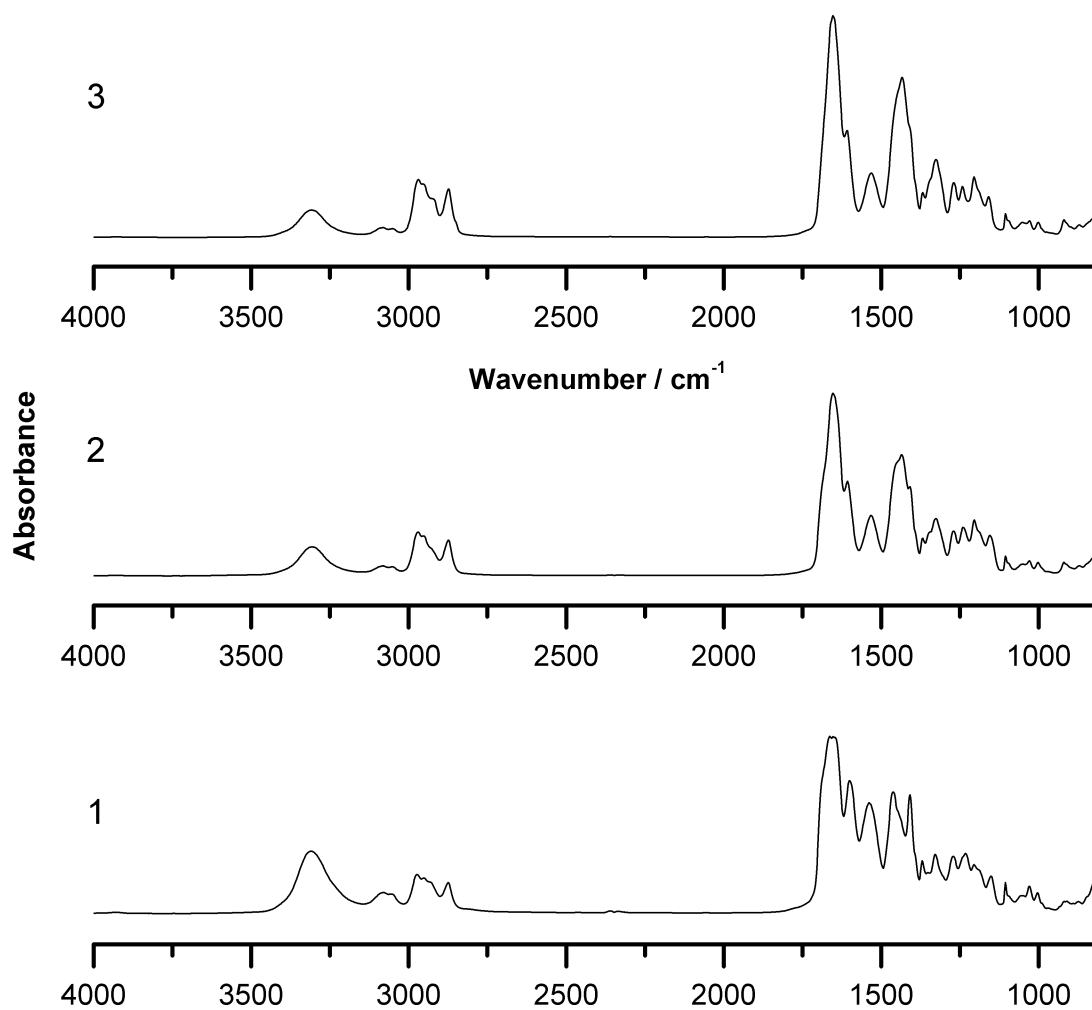
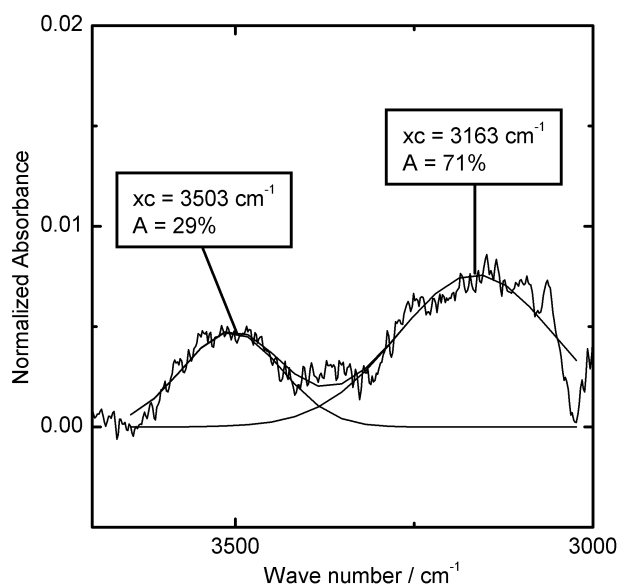*Figure 3.* IR spectra (KBr) of peptide **1 – 3**.

Figure 4. RAIRS of the Amide A region of **1**.
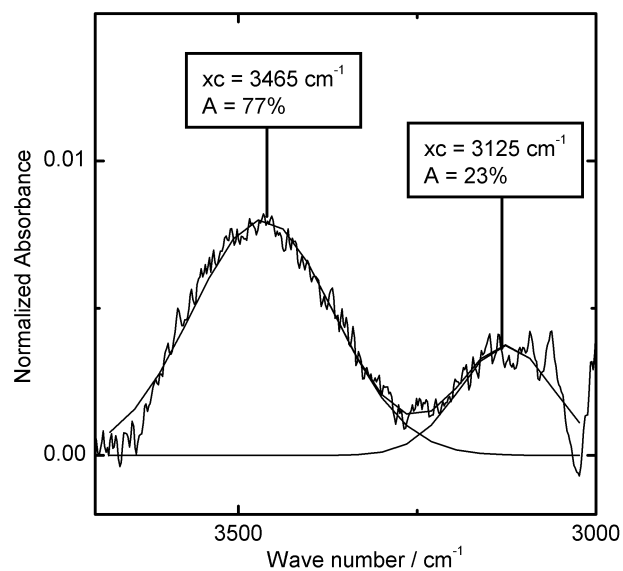

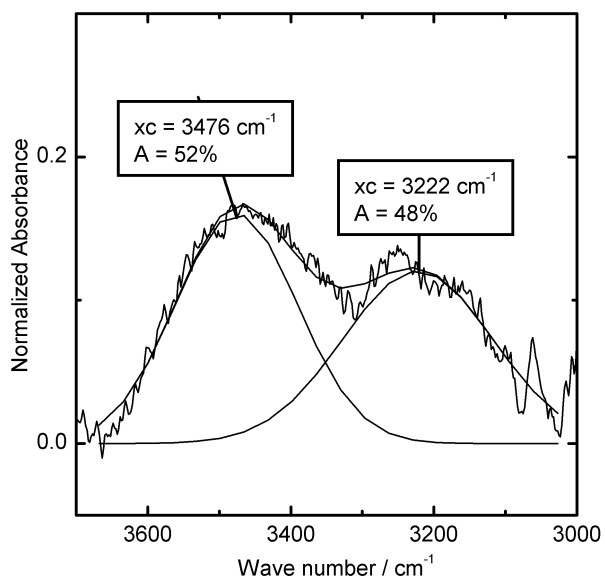*Figure 5.* RAIRS of the Amide A region of **2**.

Figure 6. RAIRS of the Amide A region of **3**.

Peptide tilt angles calculation by RAIRS.

$$D_{obs} = \frac{I_1}{I_2} = C\left(\frac{2\left[\frac{1}{2}(3\cos^2\gamma-1)\bullet\frac{1}{2}(3\cos^2\theta_1-1)\right]+1}{2\left[\frac{1}{2}(3\cos^2\gamma-1)\bullet\frac{1}{2}(3\cos^2\theta_2-1)\right]+1}\right) \tag{1}$$

D_{obs} represents the observed ratio of Amide I and Amide II absorbances and γ, θ_i and C, the tilt angle of the peptide axis from the surface normal, the angle between the transition moment (amide I amide II) and the helix axis, and the scaling constant, respectively. In case of helical peptides the transition moment from the helix axis is reported as 39° of θ_1 and 75° of θ_2, respectively.[1,2] The scaling factor, C, can be determined from the ratio of Amide I and Amide II absorbance in a KBr pellet as an approximation of a random orientation. As reported in the literature[3] for peptidic monolayers the scaling factor is approximated to 1.5.[4-6]

Collagen melting temperature determination.

Fc-peptides **1**, **2** and **3** were fit to the following general sigmoid curve shape using the following formula:

$$y = A_2 + \frac{A_1 - A_2}{1 + e^{-(x-xc)/dx}}$$

where A_2 is the fully H-bonded system and A_1 is the melted peptide. dx is a parameter that accommodates the steepness of the sigmoid and x_c is the melting temperature. Residuals were minimized using the Levenberg-Marquardt algorithm built into Origin 7.0 (OriginLab Corporation, Northampton, MA, USA).

Table 1. Parameters from CV of the Concentrated and Mixed Monolayers of Fc-peptides in 2 M $NaClO_4$ H_2O/D_2O.

Compound	ΔE (mV)		ΔE_{fwhm} (mV)	
	H_2O	D_2O	H_2O	D_2O
1	35 (10)	60 (18)	145 (8)	126 (16)
2	40 (7)	40 (15)	140 (12)	110 (10)
3	45 (10)	40 (15)	150 (15)	110 (10)
1[a]	40 (12)	30 (10)	125 (15)	95 (5)
2[a]	36 (15)	25 (10)	120 (20)	110 (10)
3[a]	40 (10)	50 (11)	130 (10)	128 (15)

[a]mixed monolayers of Fc-Peptides using hexanethiol
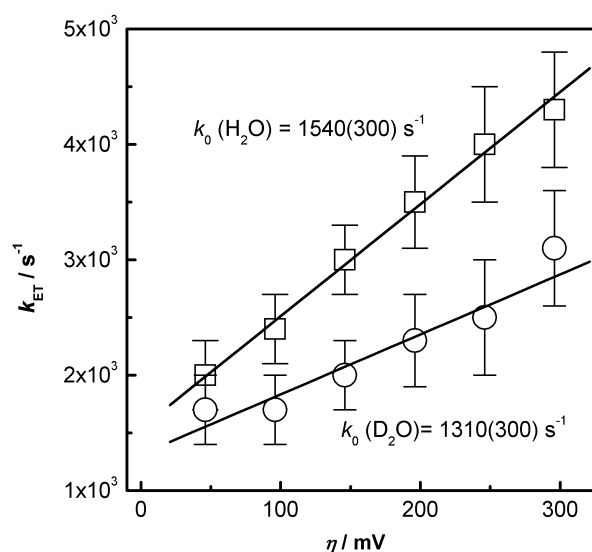

Figure 7. CA results for the calculation of k_{ET} for compound **3** in H_2O and D_2O.

Impedance CNLS fitting: The curve fitting was done using ZSimpWin software (v2.00). All parameters were permitted to float during the curve fitting process. The resultant model chosen (see Figure 4 of main text) has a χ^2 value of 0.002 on a typical data set. Of course inclusion of additional parameters resulted in a slightly lower χ^2 value(~0.001). However, we have chosen to follow the general rule that addition of a parameter should result in a 10 fold decrease in χ^2 value. Equivalent circuit models that contained 4 or fewer parameters resulted in an 8-15 fold increase in χ^2 value.

References

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