# Electron Transfer through $\alpha$ -Peptides Attached to Vertically Aligned Carbon Nanotube Arrays: A Mechanistic Transition

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# 1. General information

## General

Boc-Aib-OH, Fmoc-Aib-OH, 2-chlorotrityl chloride polystyrene resin and HATU were purchased from GL Biochem (Shanghai) Ltd., China. Dichloromethane, methanol and ethanol were purchased from Ajax Finechem Pty Ltd (Australia), N,N-dimethylformamide was purchased from Merck, Australia. Acetonitrile was purchased from Optigen Scientific. Trifluoroacetic acid and DIPEA were purchased from Sigma-Aldrich. Piperidine was purchased from Merck, Australia. All solvents and reagents were used without purification unless noted.

#### Abbreviations

Diisopropylethyl amine (DIPEA); Dichloromethane (DCM); N,N-Dimethylformamide (DMF); 2-(1H-7azabenzotriazol-1-yl)-1,1,3,3-tetramethyl uronium hexafluorophosphate methanaminium (HATU). Trifluoroacetic acid (TFA); High-performance liquid chromatography (HPLC).

#### High-performance liquid chromatography

Purification of peptide products was carried out using an HP 1100 LC system equipped with a Phenomenex C18 column (250 x 4.6 mm) for analytical traces and a Phenomenex C18 column (250 x 21.2 mm) for purification, a photodiode array detector, and a Sedex evaporative light scattering detector. Both water / acetonitrile / TFA (10 / 90 / 0.001 by v / v) and water / TFA (100 / 0.001 by v / v) solutions were used for mobile phases. For analytical traces, the gradient of water / acetonitrile / TFA phase was increased from 5% to 100% within 30 min.

#### Spectroscopic Measurements

<sup>1</sup>H NMR spectra were recorded in either CDCl<sub>3</sub> or  $Me_2SO-d_6$  solutions using a Varian Gemini-300 NMR operating at 300 MHz. Chemical shifts are reported in ppm ( $\delta$ ) with TMS (0.00 ppm) as internal standard for <sup>1</sup>H NMR. Signals are reported as follows s (singlet), d (doublet) and m (multiplet). Mass spectral data were collected on a Finnigan's LCQ mass spectrometer.

# 2. Synthesis of Peptides

# Loading Fmoc-Aib-OH onto 2-chlorotrityl chloride resin

2-Chlorotrityl chloride resin (200-400 mesh, 5.00 g) was dried under vacuum overnight and suspended in freshly distilled dichloromethane (25 mL). Fmoc-Aib-OH (2.50 g) was dried *in vacuo* for 24 h and dissolved in anhydrous dichloromethane (15 mL) to which was added DMF (0.5 mL). The Fmoc-Aib-OH / DCM solution was poured into the resin suspension followed by the addition of DIPEA (5 mL). The resin and solution were stirred gently at rt overnight and then transferred to a sintered funnel fitted with a Teflon stopcock. The resin was drained and rinsed with DCM (3 x 50 mL), DMF (3 x 50 mL), and again with DCM (3 x 50 mL). In order to cap any unreacted 2-chlorotrityl chloride linker, the resin was treated

with a solution of DCM, methanol and DIPEA (17 : 2 : 1 respectively, 2 x 30 min). The resin was rinsed successively with DCM (3 x 50 mL), DMF (3 x 50 mL), and DCM (3 x 50 mL) and then dried in vacuo over night, to give 6.52 g Aib loaded resin (Fmoc-Aib-OH loading = 0.72 mmol  $g^{-1}$ ).

## Synthesis of N-terminal ferrocene-derivatised oligopetides (H<sub>2</sub>N-Aib<sub>n</sub>-Fc)

Fmoc-Aib-OH loaded 2-chlorotrityl chloride resin (2.00 g) was transferred into a sintered funnel fitted with a Teflon stopcock, and then rinsed with DCM ( $2 \times 20$  mL). Resin loading was typically 0.5 mmol/ gram of resin. After air drying, the Fmoc group was removed by reaction with a solution of 25% piperidine in DMF (20 mL) for 30 min followed by washing successively with DCM (3 x 20 mL), DMF (3 x 20 mL), and DCM (3 x 20 mL). To a solution of Fmoc-Aib-OH (1.00 g, 2 equiv) in DMF (4 mL) was added a 0.5 M solution of HATU in DMF (2 mL) followed by DIPEA (1.2 mL, 4-fold excess) and the resulting solution was added to the deprotected resin. The mixture was left for 2 h, with occasional stirring. The resin was isolated by filtration and rinsed successively with DCM (3 x 50 mL), DMF (3 x 50 mL), and DCM (3 x 50 mL). The sequence was repeated 2 more times to ensure complete coupling. Successive additions of Fmoc Aib-OH were carried out, using this protocol, to give the appropriate oligopeptide. Each peptide was capped with Boc-Aib-OH in the last cycle using the same protocol and the oligopeptides cleaved from the resin with 2% TFA / DCM (v/v). The crude products were purified by HPLC, with retention times shown in Table S1.

Table S1. HPLC reten	Table S1. HPLC retention time from analytical traces							
Peptide name	Retention time (min)							
Boc-Aib-OH	14.13							
Boc-Aib <sub>2</sub> -OH	15.05							
Boc-Aib <sub>3</sub> -OH	16.87							
Boc-Aib <sub>4</sub> -OH	18.48							
Boc-Aib₅-OH	20.69							

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Each Boc-Aib<sub>n</sub>-OH peptide (1.05 equiv) was then added to a solution of ferrocenylmethylamine 1, 2(50mg) in DMF (2 mL) followed by a 0.5 M solution of HATU in DMF (2 mL, 4 equiv) and DIPEA (4 equiv). The solution was stirred gently at rt for 24 h and volatiles removed in vacuo. Each oligopeptide was purified by HPLC with retention times shown below in Table S2.

Peptide name	Retention time (min)							
Boc-Aib-Fc	25.38							
Boc-Aib <sub>2</sub> -Fc	25.66							
Boc-Aib <sub>3</sub> -Fc	26.99							
Boc-Aib <sub>4</sub> -Fc	28.67							
Boc-Aib <sub>5</sub> -Fc	30.77							

**Table S2.** HPLC retention time from analytical traces

To a solution of the thus purified Boc-Aib<sub>n</sub>-Fc oligopeptide (100 mg), in trifluroethanol (5 mL), was added a 4M solution of HCl in dioxane (1 mL). The reaction mixture was stirred for 15 min at rt and the solvent removed *in vacuo*. The peptide was purified by HPLC with retention times shown in Table S3 and a representative trace for H<sub>2</sub>N-Aib<sub>5</sub>-Fc shown in Figure S1 below.

Peptide name	Retention time (min)
Ferrocenylmethylamine	11.73
H <sub>2</sub> N-Aib-Fc	13.35
H <sub>2</sub> N-Aib <sub>2</sub> -Fc	13.82
H <sub>2</sub> N-Aib <sub>3</sub> -Fc	14.57
H <sub>2</sub> N-Aib <sub>4</sub> -Fc	15.98
$H_2N-Aib_5-Fc$	17.36

#### Table S3. HPLC retention time from analytical traces



Figure S1. Representative HPLC trace for H<sub>2</sub>N-Aib<sub>5</sub>-Fc

**H**<sub>2</sub>**N**-**Aib**-**Fc**, <sup>1</sup>H NMR (300MHz; CDCl<sub>3</sub>) δ 7.26 (s, 1H, 1NH), 4.19 (m, 5H, Cp), 4.17 (m, 2H), 4.13 (m, 2H), 4.07 (d, 2H, CH<sub>2</sub>), 1.40 (s, 6H, 2 βCH<sub>3</sub>). MS:  $[M+Na]^+_{calcd} = 323.2$ ,  $[M+Na]^+_{found} = 323.2$ .

**H**<sub>2</sub>**N**-**Aib**<sub>2</sub>-**Fc**, <sup>1</sup>H NMR (300MHz; DMSO) δ 8.14 (s, 1H, NH), 7.78 (s, 1H, NH), 4.30 (m, 9H, C<sub>10</sub>H<sub>9</sub>Fe), 3.86 (d, 2H, CH<sub>2</sub>, 1.56 (s, 6H, 2 βCH<sub>3</sub>), 1.24 (s, 6H, 2 βCH<sub>3</sub>); MS:  $[M+Na]^{+}_{calcd} = 408.3$ ,  $[M+Na]^{+}_{found} = 408.2$ .

**H**<sub>2</sub>**N**-**Aib**<sub>3</sub>-**Fc**, <sup>1</sup>H NMR (300MHz; DMSO) δ 8.18 (s, 1H, NH), 7.70 (s, 1H, NH), 7.40 (s, 1H, NH), 4.30 (m, 2H), 4.21 (m, 5H, Cp), 4.10 (m, 2H), 3.93 (d, 2H), 1.50(s, 6H, 2 βCH<sub>3</sub>), 1.39(s, 6H, 2 βCH<sub>3</sub>), 1.37 (s, 6H, 2 βCH<sub>3</sub>); MS:  $[M+Na]^+_{calcd} = 493.4$ ,  $[M+Na]^+_{found} = 493.3$ .

**H**<sub>2</sub>**N**-**Aib**<sub>4</sub>-**Fc**, <sup>1</sup>H NMR (300MHz; DMSO) δ 8.47 (s, 1H, NH), 8.25 (s, 1H, NH), 7.62 (s, 1H, NH), 7.22 (s, 1H, NH), 4.30 (m, 2H), 4.13 (m, 5H, Cp), 4.00 (m, 2H), 3.91 (d, 2H, CH<sub>2</sub>), 1.58 (s, 6H, 2 βCH<sub>3</sub>), 1.38 (s, 6H, 2 βCH<sub>3</sub>), 1.29 (s, 6H, 2 βCH<sub>3</sub>), 1.28 (s, 6H, 2 βCH<sub>3</sub>); MS:  $[M+Na]^+_{calcd} = 578.5$ ,  $[M+Na]^+_{found} = 578.5$ .

**H**<sub>2</sub>**N**-**Aib**<sub>5</sub>-**Fc**, <sup>1</sup>H NMR (300MHz; DMSO) δ 8.44 (s, 1H, NH), 8.07 (s, 1H, NH), 7.91 (s, 1H, NH), 7.76 (s, 1H, NH), 7.24 (s, 1H, NH), 4.27 (m, 2H), 4.21 (m, 5H, Cp), 4.17 (m, 2H), 4.05 (d, 2H, CH<sub>2</sub>), 1.52 (s, 6H, 2  $\beta$ CH<sub>3</sub>), 1.33 (s, 6H, 2  $\beta$ CH<sub>3</sub>), 1.32 (s, 6H, 2  $\beta$ CH<sub>3</sub>), 1.25 (s, 6H, 2  $\beta$ CH<sub>3</sub>), 1.23 (s, 6H, 2  $\beta$ CH<sub>3</sub>); MS: [M+Na]<sup>-</sup> calcd = 663.6, [M+Na]<sup>-</sup> found = 663.5.

# 3. Geometry of N- ferrocene-oligopetides

The ROESY spectra (600 MHz) of  $H_2N-Aib_3$ -Fc (Figure S2),  $H_2N-Aib_4$ -Fc (not shown), and  $H_2N-Aib_5$ -Fc (Figure S3) show characteristic cross-peaks between NH and Me that are consistent with a folded helical conformation as for related (Aib)<sub>n</sub> oligopeptides<sup>3-7</sup>.



**Figure S2**. ROESY spectrum of  $H_2N$ -Aib<sub>3</sub>-Fc in Me<sub>2</sub>SO-d<sub>6</sub> (peptide concentration: 18 mM). The red arrow shows the important correlations.



**Figure S3**. ROESY spectrum of  $H_2N$ -Aib<sub>5</sub>-Fc in Me<sub>2</sub>SO-d<sub>6</sub> (peptide concentration: 16 mM). The cross-peaks consistent with a folded structure are indicated.

#### Molecular modelling and hydrogen bonding of ferrocene-derivatised oligopeptides

Molecular geometries of peptides were optimised by the hybrid B3LYP method with  $6-31G^{**}$  basis set, as implemented in Gaussian 09 with tight convergence criteria <sup>8</sup>. The optimised geometries, edge-to-edge distance and number of hydrogen bonds are listed in Table S4. The number of hydrogen bonds is consistent with  $3_{10}$ -helical peptides bearing a terminal ferrocenyl group<sup>6</sup>.

Aib	Optimised structure	Intramolecular
No.		H-Bond
		Number
0	Distance : 4.36 Å	0
1	Distance : 5.37 Å	0
2	Distance : 6.39 Å	0
3		1
	Distance : 9.93 Å	

Table	<b>S4</b> .	The	optimised	geometries,	edge-to-edge	distance	and	number	of	hydrogen	bonds	for
ferroc	enyl	methy	ylamine and	d ferrocene-d	erivatised oligo	peptide						



# 4. Preparation of SWCNTs/Si arrays<sup>9, 10</sup>

The SWCNTs/Si nanostructures were prepared as previously reported.<sup>10</sup> Highly boron doped p-type silicon (100) surfaces (0.5×0.5 cm<sup>2</sup> size, 0.5 mm thickness, 1 m $\Omega$  cm resistivity and purchased from Virginia Semiconductor, Inc. USA) were ultrasonically cleaned in acetone (99.5%, Merck) for 30 seconds and flushed with copious amounts of Milli Q water (18 M $\Omega$  cm). The silicon pieces were then immersed first into a 1:1:5 mixture of 30% NH<sub>4</sub>OH (Sigma-Aldrich), 30% H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich) and Milli Q water (18  $M\Omega$  cm) for 15 mins at 80 °C, followed by immersion into a 1:1:5 mixture of 36% HCl (Ajax Finechem), 30% H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich) and Milli Q water (18 M $\Omega$  cm) for 15 mins at 80 °C. The hydroxyl terminated silicon was incubated in a DMSO (99.9%, ACS Spectrophotometric Grade, Sigma-Aldrich) solution containing both 0.1 mg mL<sup>-1</sup> dicyclohexyl carbodiimide (DCC, 99%, Aldrich) and 0.12 mg mL<sup>-1</sup> functionalised carbon nanotubes. The nanotubes (P2-SWCNTs purchased from Carbon Solutions, Inc. USA) were cut for 8 hrs in mixed HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> acid to give an average length of 360 nm with 4% (mole percent) carboxylic acid groups <sup>11, 12</sup> and suspended in DMSO. The silicon substrates were exposed to the nanotube solution overnight to give an average separation of 50 nm between carbon nanotube bundles, which is significantly greater than the lengths of attached peptides <sup>9-11, 13</sup>. This negates the possibility of shortcuts between the ferrocenyl end of peptide and the wall of a neighbor SWCNT. The samples were then rinsed with copious amounts of acetone to remove any unbound reagents. According to information provided by the Carbon Solution Inc, the single-walled carbon nanotubes (SWCNTs) are synthesised by electric arc discharge using nickel/yttrium catalyst. The individual singlewalled carbon nanotubes have a length distribution between 0.5 and 3.0 µm and an average diameter of

1.4 nm with a ratio of 2 between semiconducting to metallic SWCNTs. The thus prepared SWCNTs were purified by air oxidation with a subsequent treatment in acid to produce P2-SWCNTs product.

# 5. Attachment of ferrocene-oligopeptide to SWCNTs/Si arrays<sup>13</sup>

SWCNTs-Si structures were incubated in a DMF solution containing 0.01 mol L<sup>-1</sup> ferrocene-derivatised oligopeptide (or ferrocenylmethylamine), 0.1 mol L<sup>-1</sup> HATU and 0.1 mol L<sup>-1</sup> DIPEA for 24 hours at room temperature. The resulting surfaces were rinsed in turn with DMF and DCM and finally washed with copious DCM to remove any physically absorbed chemicals, then stored in the dark for electrochemical measurement after being dried by a high purity nitrogen stream. To measure the physical absorption of peptides on nanotubes, control samples were prepared using the same procedure without the addition of HATU and DIPEA to the incubating solution. The use of nanotube arrays provides rough surfaces, the bonding sites of which can accommodate large amounts of ferrocene-oligopeptide to give a densely packed surface.

# 6. Characterisation of modified SWCNTs/Si arrays with attached ferroceneoligopeptides

#### Infrared spectroscopy

The FTIR spectra of ferrocene-derivatised oligopeptide modified SWCNTs/Si were acquired at the reflection mode by Nicolet iN10MAX FTIR Microscope (thermal scientific, USA) equipped with a MCT (mercury cadmium telluride) detector cooled with liquid nitrogen. A SWCNTs/Si surface was used as the reference. All of the spectra were recorded at room temperature by integrating 256 scans with a resolution of 4 cm<sup>-1</sup>. The chamber was purged with dry N<sub>2</sub> during data acquisition. Figure S4 shows the FTIR spectra for Aib3-Fc and Aib5-Fc. Amide I and II bands were observed at 1668 and 1538 cm<sup>-1</sup> for Aib3-Fc, Aib4-Fc (not shown) and Aib5-Fc. There wavenumbers are characteristic for helical conformation <sup>7, 14, 15</sup>. By contrast Aib1-Fc and Aib2-Fc revealed absorption bands at 1710 cm<sup>-1</sup>. Thus the helical conformations for Aib3-Fc, Aib4-Fc and Aib5-Fc remain intact after surface immobilisation onto SWCNTs/Si arrays. The rigidity of the constrained helices further restricts rotation about the C-N bond. This negates the possibility of electrochemical shortcuts between the peptide and supporting SWCNT.



**Figure S4**. Reflective FTIR spectra for Aib3-Fc (a) and Aib5-Fc (b) after their surface immobilisation onto SWCNTs/Si arrays.

#### Characterisation of vertically aligned SWCNTs/Si arrays

The vertically aligned carbon nanotubes array/Si surfaces have previously been well-characterised by a range of surface techniques, such as AFM, SEM, IR, XPS and Raman<sup>9-11, 13, 16-18</sup>. The electrochemical results indicate that SWCNTs/Si electrodes possess a sufficient density of states to support relatively rapid electron transfer kinetics <sup>10</sup>. Due to the significantly small size of peptide (1.4 nm in length for Aib5-Fc) in comparison with individual SWCNT (average length of 360 nm), AFM is not capable of providing clear demonstration for the immobilisation of peptides on SWCNTs/Si. This conclusion has been stated in our early publication <sup>9, 13</sup>. Nevertheless IR data confirmed that longer peptides (n=3-5) remain helical structure after immobilisation (as shown in Figure S4). The electrochemical applications of SWCNTs/Si nanostructure have been documented, including photovoltaic devices<sup>9, 19-22</sup>, biosensors<sup>23-25</sup>, molecular electronics <sup>9, 13, 18, 26</sup> and field-emission devices<sup>27</sup>.

# 7. Electrochemistry

All electrochemical experiments were carried out in a specially designed electrochemical cell shown in Figure S5. This provides a very small working electrode area. The RC time constant of the electrochemical cell can then be shortened considerably so that fast kinetic events are accurately measured. Compared to the conventional electrochemical cell <sup>28</sup>, the system described here has some distinct advantages, such as the simplicity, low fabrication cost, and the application of a three electrode system. The electrical contact to the working electrode was maintained by scratching the unpolished side of the wafer with a SiC crystal, and adhering freshly polished aluminium foil well to the scratched side. A polypropylene pipette (~1 mL) tip, containing a platinum wire counter electrode, a bare silver wire (Ag/AgCl) reference electrode and electrolyte solution, was pressed down against the silicon samples. The Ag/AgCl reference electrode was calibrated after each experiment against the ferrocene/ferricenium couple. All potentials are reported against the KCl saturated calomel electrode (SCE), using  $E^{\circ}_{Fc/Fc+} = 0.464$  V versus SCE. 0.1 mol L<sup>-1</sup> tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Sigma) / CH<sub>3</sub>CN (Isocratic HPLC grade, Scharlau Chemie) solutions is used as the electrolyte. The working area was determined by electrochemical scans in 0.1 mmol  $L^{-1}$  ferrocene/0.1 mol  $L^{-1}$ TBAPF<sub>6</sub>/CH<sub>3</sub>CN solution ( $D_{0, Fc}$ =2.3×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1 29, 30</sup>). All chemicals were used as-received. All electrochemical experiments were performed inside a dry-box filled with high purity  $N_2$  using a computer controlled PGSTAT100 electrochemical workstation (Autolab, Netherlands) with ohmic-drop correction at room temperature.



**Figure S5**. Schematic diagram of the specially designed electrochemical cell. (1) Modified retort stand, (2) Aluminium foil, (3) Silicon working electrode, (4) Organic electrolyte, (5) Polypropylene pipette, (6) Platinum wire winding counter electrode, (7) PTFE tubing for insulation between silver and platinum wire, (8) Bare silver wire reference electrode

#### Electrochemical data analysis

Figure S6 shows a series of cyclic voltammograms of ferrocene-derivatised oligopeptide with different number of Aib modified SWCNTs / Si electrode in 0.1 mol  $L^{-1}$  tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) / CH<sub>3</sub>CN solution.



**Figure S6**. Cyclic voltammograms of ferrocene-derivatised oligopeptide with different number of Aib modified SWCNTs / Si electrode in 0.1 mol L<sup>-1</sup> tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) / CH<sub>3</sub>CN solution, with the scan rate, *v*, of 5, 10, 20, 50, 100, 200 and 500 mV/s from the centre to upright, (a) Fc, (b) Aib<sub>1</sub>-Fc, (c) Aib<sub>2</sub>-Fc, (d) Aib<sub>3</sub>-Fc and (e) Aib<sub>4</sub>-Fc.

After background subtraction, the surface concentration of ferrocene-derivatised oligopeptide can be determined using the areas under the oxidation/reduction peaks of the cyclic voltammogramms as described by Laviron's theory <sup>31</sup>.

$$i_p = \frac{n^2 F^2 A \Gamma v}{4RT} = \frac{n F Q v}{4RT} \quad (S1)$$

where  $i_p$  is the peak current (A),  $\Gamma$  is the surface concentration (mol cm<sup>-2</sup>), A is the electro-active area (cm<sup>2</sup>), Q is the peak area of the voltammogram (C), and n is the number of electrons involved. Surface concentrations for ferrocene-derivatised oligopeptides and ferrocenylmethylamine were shown in Table 1.

Figure S7 shows the dependence of  $E_p$  on  $\ln(v)$  determined from cyclic voltammograms of ferrocenederivatised oligopeptide with different number of Aib modified SWCNTs / Si. The apparent rate constant of electron transfer can be calculated using Laviron's formalism <sup>31</sup>.

$$E_{p} = E^{o'} + \frac{RT}{\alpha nF} \ln \frac{RTk_{app}}{\alpha nF} - \frac{RT}{\alpha nF} \ln v \quad (S2)$$

where  $\alpha$  is the transfer coefficient,  $k_{app}$  the apparent rate constant of electron transfer, v the scan rate, and  $E^{o'}$  is the formal potential. Electron transfer rate constants and formal potentials of ferrocenylmethylamine and ferrocene-derivatised oligopetides are shown in Table 1.



**Figure S7**. The dependence of  $E_p$  on  $\ln(v)$  determined from cyclic voltammograms of ferrocenederivatised oligopeptide with different number of Aib modified SWCNTs / Si electrode in 0.1 mol L<sup>-1</sup> tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) / CH<sub>3</sub>CN solution.

# 8. Discussions on the roles of SWCNT and Si surface in the electron transfer process

Based on the experimental design, an oxidation of the surface modified ferrocene moiety involves several sequential electron transfer steps. Firstly an electron from the ferrocene transfers to the bridge of the Aib sequence, then injects into and down the bound single walled carbon nanotube, with possibly hopping to another nanotube, before eventually reaching the silicon surface. For a reduction of the surface modified ferrocene moiety, the electron transfer process follows these sequential steps in reverse. Unlike previous studies on donor-bridge-acceptor systems, we have considered these steps because of the heterogeneity of the paths that an electron transferred from a peptide bridge to a carbon nanotube must follow to reach the electrode. However, we have shown that the electron transfer rates for these additional steps are much faster than electron transfer across the peptide bridge in our system, and therefore they can be safely ignored in the analysis of the data.

The rate constant for a single electron transferring through the silicon substrate or between the ends of a carbon nanotube can be estimated from  $^{32}$ 

$$k = \frac{A \cdot \Delta V}{e \cdot \rho \cdot l} \tag{S3}$$

where *I* is the distance over which the electron is transferred (the thickness of the silicon substrate or length of the nanotube),  $\Delta V$  is the voltage drop across this distance, *e* is the elementary charge,  $\rho$  is the resistivity of the material, and *A* is the cross-sectional area of the material through which the electron is transferred. As a lower bound for the voltage drop, we have chosen  $\Delta V=1$  mV, which is within the potential drift of the electrochemical experiments. The silicon substrate was contacted via a large-area aluminium foil as the current collector. For the silicon substrate, *A* was taken to be the working area used in the electrochemical measurements defined by the functionalised surface in contact with electrolytic solution; for the carbon nanotubes, it was taken as the nanotube diameter. The electron transfer rate constants through the silicon substrate and metallic and semiconducting single-walled carbon nanotubes used in this study are listed in Table S5.

Electron transfer	Resistivity	Cross-sectional	Electron	Electron transfer					
medium		area	transfer	rate constant					
			distance						
Silicon surface	1 m $\Omega$ cm	0.6 mm	0.5 mm	3.52×10 <sup>17</sup> s <sup>-1</sup>					
	at room temperature								
Metallic SWCNTs	10 <sup>-4</sup> $\Omega$ cm at 300 K $^{ m 33}$	1.4 nm	360 nm	2.67×10 <sup>17</sup> s <sup>-1</sup>					
Semiconducting	$3.3 \times 10^{-7} \Omega$ cm	1.4 nm	360 nm	$1.04 \times 10^{13} \text{ s}^{-1}$					
SWCNTs	at room temperature $^{st}$								

**Table S5.** Electron transfer rate constants in silicon surfaces, individual metallic and semiconductingSWCNTs, calculated using eq S3.

\* Note: Fuhrer and co-workers <sup>34</sup> reviewed the resistivity and charge-carrier mobility in semiconducting carbon nanotubes. For the calculation, a moderate one-dimensional conductivity of  $4.6 \times 10^{-8}$  S cm at room temperature is selected. The one-dimensional conductivity is converted to the resistivity of  $3.3 \times 10^{-7} \Omega$  cm using the SWCNT diameter of 1.4 nm.

McEuen and co-workers <sup>35</sup> reported that both metallic–metallic and semiconducting–semiconducting crossed nanotube junctions have high conductances. However for a metallic–semiconducting crossed junction, charge depletion leads to the formation of a rectifying Schottky barrier and a lower conductance compared with the metallic–metallic and semiconducting–semiconducting cases. Roth and co-wokers have measured current–voltage curves for metallic–semiconducting crossed SWCNT junctions as a function of temperature. They fit their results to conventional thermionic emission theory, in which the reverse saturation current density is given by <sup>36</sup>

$$J_o = A^* T^2 \exp\left(-\frac{qV_{bo}}{k_B T}\right) \quad \text{(S4)}$$

Here  $A^*$  is the Richardson constant corresponding to the effective mass of the charge carriers,  $A^* = 4\pi q m^* k_B^2/h^3$ , where  $m^*$  is the effective mass of electron in the material<sup>37</sup>. *T* is the absolute temperature, *q* is the charge of electron,  $k_B$  is the Boltzmann constant and *h* is Planck's constant. Taking  $m^*$  for the nanotubes to be 0.05m\* of the effective mass in a graphene sheet, the experimental results were well-fit with a junction barrier  $V_{bo}$  of -0.08 V at most temperatures<sup>36</sup>. From these parameters,  $J_0$  is obtained as  $2.45 \times 10^8$  A cm<sup>-2</sup> at 300K. Since the current through a rectifying junction is greater in magnitude than  $J_0$  for almost all applied voltages, we can use  $J_0$  for a metallic–semiconducting crossed SWCNT junction at this temperature as the lower bound for the current density between two nanotubes and thereby estimate the minimum electron transfer rate between two nanotubes in our study. The rate constant for a single electron transferring through the metallic–semiconducting crossed nanotube junction can be estimated as by using the reported junction area (on the order of 1 nm<sup>2</sup>) <sup>35</sup>,

$$k = \frac{J_o A}{e} = \frac{2.45 \times 10^9 A \cdot m^{-2} \times 1 \ nm^2}{1.6 \times 10^{-19} C} = 1.53 \times 10^9 s^{-1}$$
 (S5)

It should be noted that the carbon nanotubes in our studies formed bundles via a strong self-adhesion. So the contact area is significantly larger than that of a crossed junction, by about 2 orders of magnitude. By taking into account of these issues, the rate constant between metallic and semiconducting nanotubes should be on the order of  $10^{11}$  s<sup>-1</sup>.

Though the electron transfer process in this system involves several sequential electron transfer steps, all above calculations have shown that the electron transfer rate constant in the peptides is 8 orders of magnitude slower than for all other electron transfer steps in the overall process. The electron transfer through the bridges of Aib sequences is obviously the rate-limiting step. Therefore the electron transfer rate constants reported in the study only reflect the impact of Aib sequences.

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