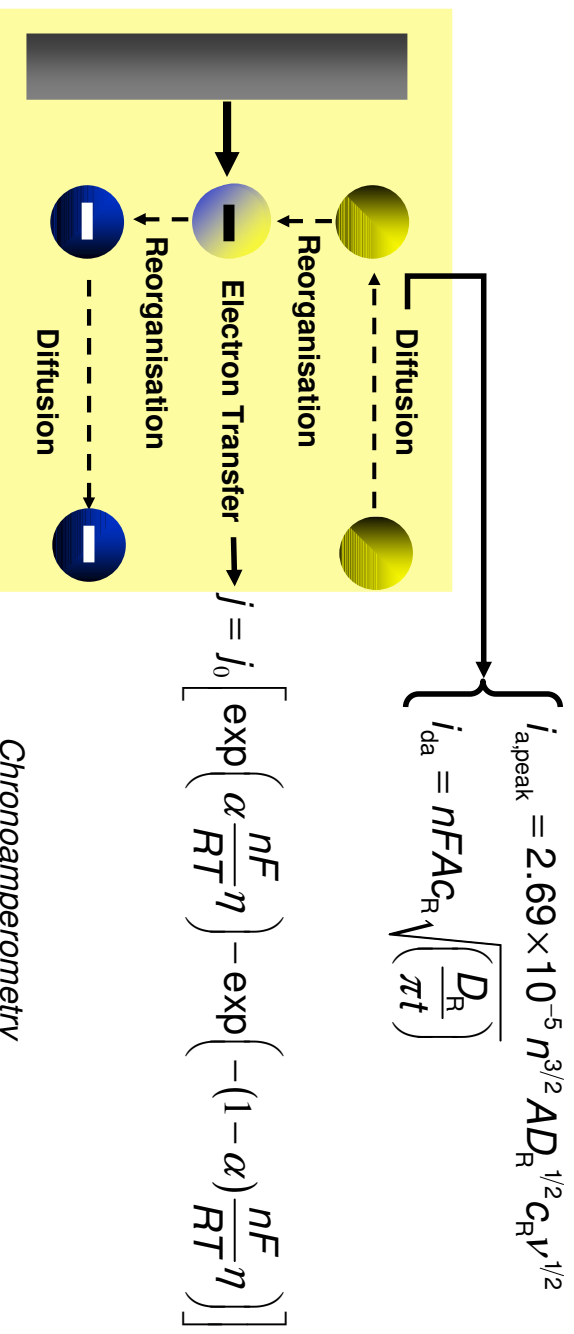


# Previously on Electrochemistry



Rotating disc electrodes

Ultramicroelectrodes

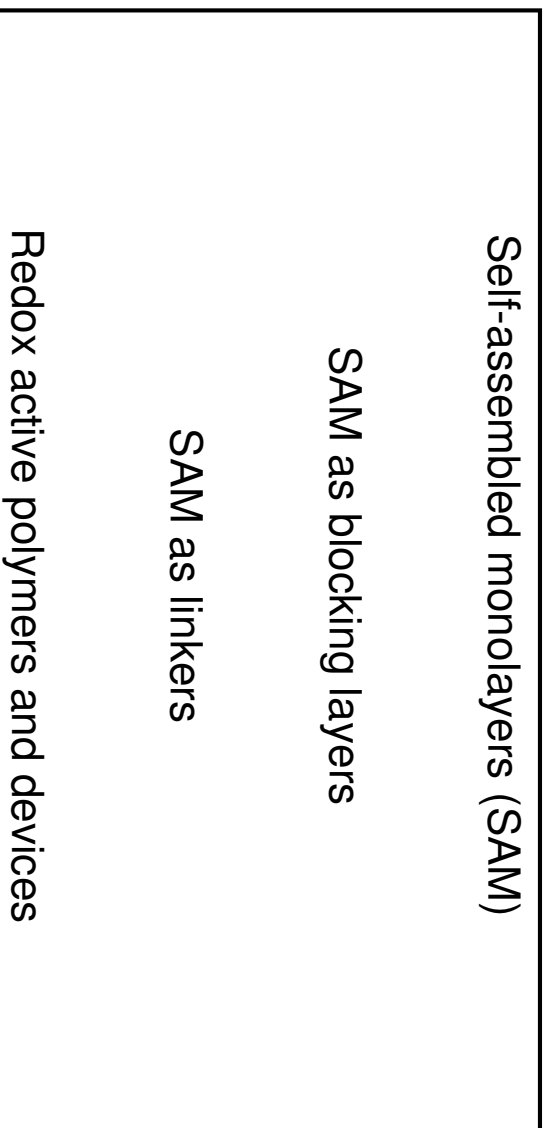
Chronoamperometry

Chronocoulometry

Cyclic Voltammetry

89

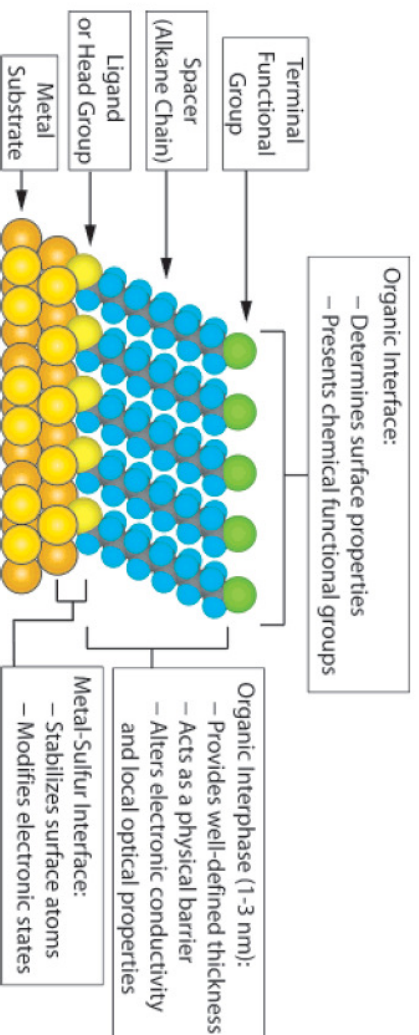
## Electroactive Layers and Modified Electrodes



90

## 5.1 Self-assembled monolayers (SAM)

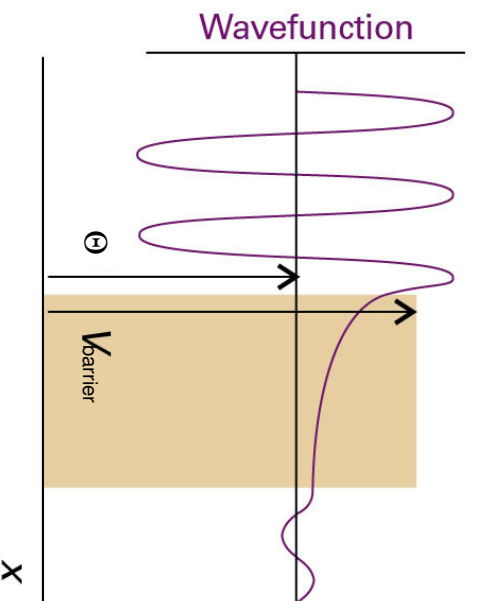
- Protecting/blocking the electrode surface – corrosion inhibitors, selective sensors
- Bridging higher order molecular architectures – Sensors
- Manipulating charge transport kinetics/reactivity – molecular electronics



**Fig. 5.1** Schematic representation of a SAM (organosulfur type) at a metal surface [Love et al., Chemical Reviews 105 (2005) 1103].

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## 5.2 SAM as blocking layers



**Fig. 5.3** A particle with energy  $E$  and mass  $m$  incident on the left side of a barrier of energy  $V_{\text{barrier}}$ . Inside the barrier there are no oscillations. At the other side the barrier, the wavefunction is non-zero and oscillations are observed again. Only the real component of the wavefunction is shown [Atkins 2002].

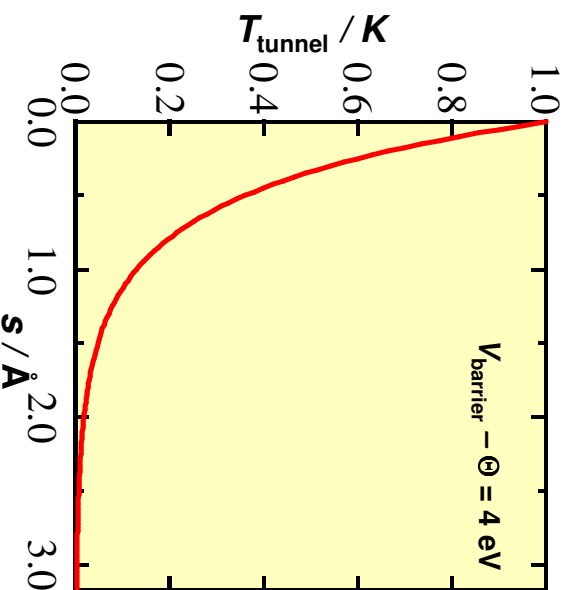
92

The transmission probability  $T_{\text{tunnel}}$ ,

$$T_{\text{tunnel}} = \frac{16k^2\kappa^2}{(k^2 + \kappa^2)} \exp(-2\kappa s) = K \exp(-2\kappa s) \quad \text{eqn. 5.1}$$

$$\kappa = \frac{\sqrt{2m(V_{\text{barrier}} - \Theta)}}{\hbar}$$

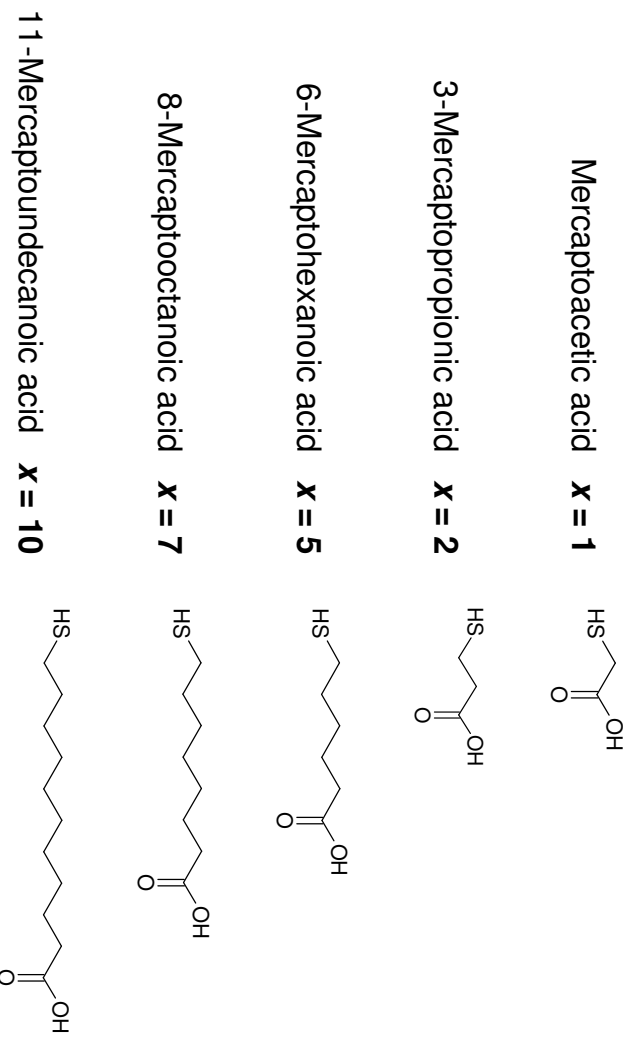
$$\kappa^2 = \frac{2m\Theta}{\hbar^2}$$



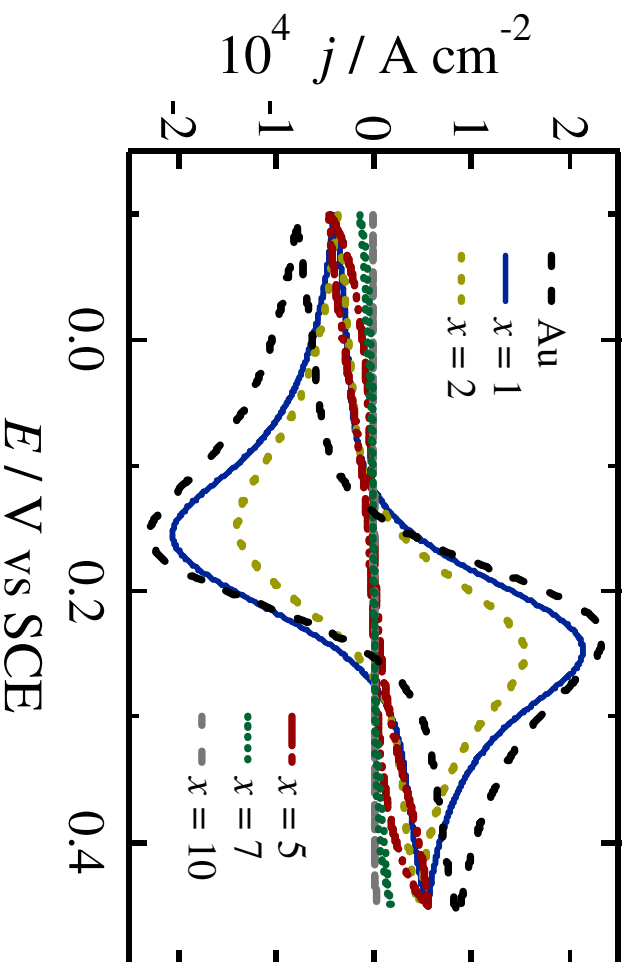
**Fig. 5.4** Characteristic distance dependence of the transmission probability of an electron.

93

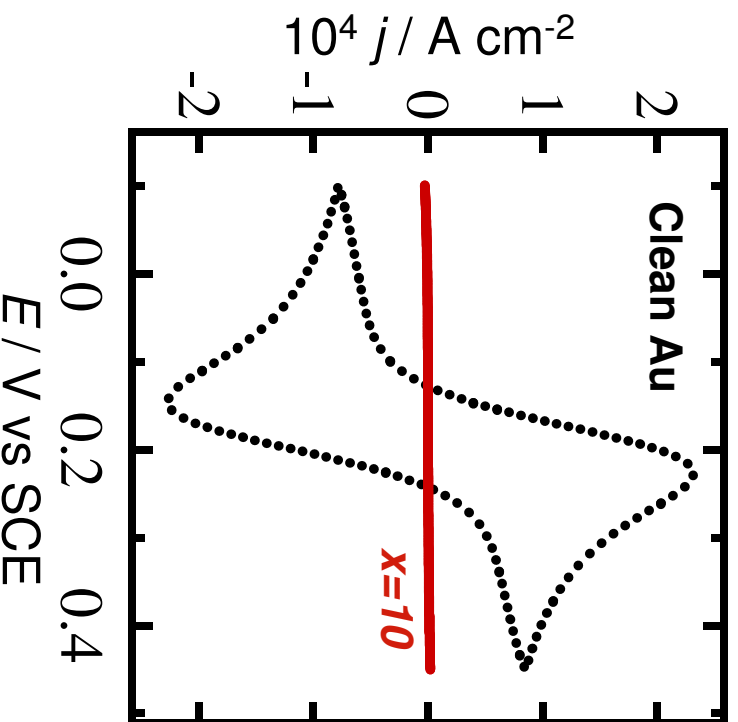
Carboxyl terminated alkyl thiolate self-assembled monolayer,



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**Fig. 5.5** Cyclic voltammograms of the ferriferrocyanide couple on Au electrodes modified by carboxyl-terminated alkane thiols (fig.5.4). The scan rate was 50 mV s<sup>-1</sup>. The concentration of each redox species is 5.0×10<sup>-4</sup> mol dm<sup>-3</sup>. (Bradbury, J.Phys.Chem 95(2008))



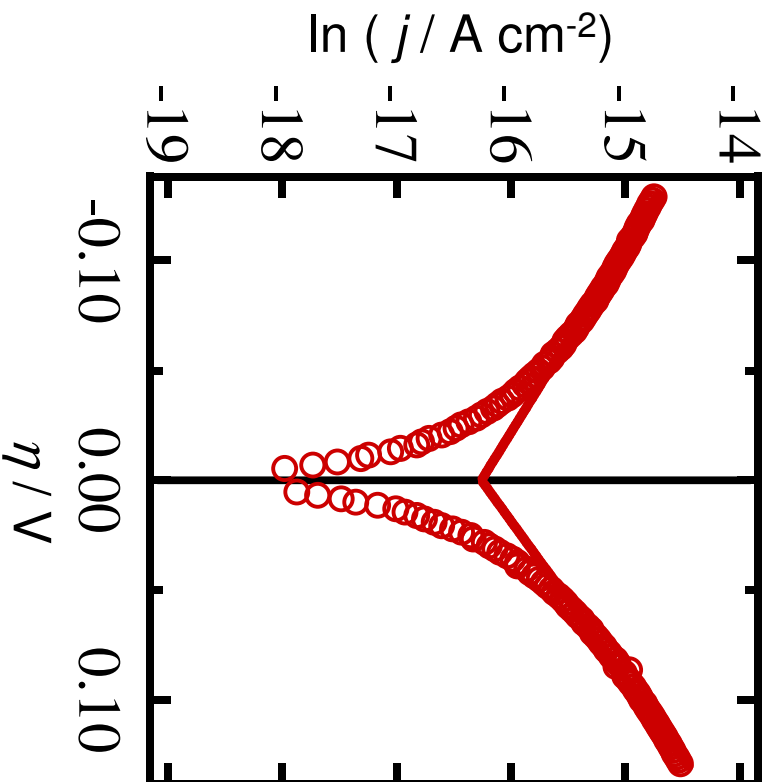
**Clean Au**

$$\Delta E_{\text{peak}} = 59 \text{ mV}$$

$$j_{\text{Au,peak}} = 2.69 \times 10^{-5} n^{3/2} D_R^{1/2} C_R V^{-1/2}$$

Diffusion controlled process

**Fig. 5.6A** Blocking effect of the SAM  $x = 10$  on the redox process at Au electrodes.. Experimental conditions as in fig. 5.5 (Zhao, J.Phys.Chem B 2005)



**$x=10$**

$\alpha \approx 0.5$

$j_0^{\text{MUA}} = (1.2 \pm 0.4) 10^{-7} \text{ A cm}^{-2}$

ET controlled process

**Fig. 5.6B** Tafel plot of the MUA ( $x=10$ ) modified electrode. Experimental conditions as in fig. 5.5 (Zhao, J.Phys.Chem B 2005)

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Based on eqn. 5.1, the standard electron transfer rate constant:

$$k^{\ominus}(x) = k^{\ominus}(0) \exp(-\beta x) \quad \text{eqn. 5.3}$$

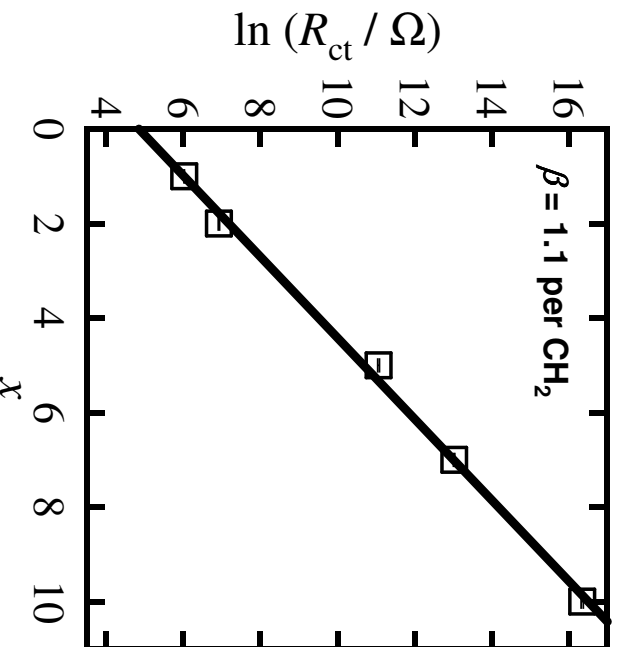
$\beta$  is the tunnelling attenuation constant

The charge transfer resistance  $R_{\text{ct}}$  (eqn. 2.13),

$$R_{\text{ct}} = \frac{RT}{nFj_0} = \frac{RT}{n^2 F^2 k^{\ominus} C_{\text{redox}}} \quad \text{eqn. 5.4}$$

Eqn. 5.3 and 5.4,



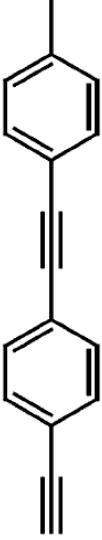
$$R_{\text{ct}}(x) = R_{\text{ct}}(0) \exp(\beta x) \quad \text{eqn. 5.5}$$



The thickness of the thiol layer is linearly dependent on the number of methylene units. In this case,  $\beta \sim 0.8 \text{ \AA}^{-1}$ .

**Fig. 5.7** Charge transfer resistance for the ferri/ferrocyanide couple as a function of the number of methylene groups in the SAM. Surface area of the electrode is  $0.07 \text{ cm}^2$ . Other parameters as in figure 5.5. (Bradbury, J. Phys. Chem C 2008)

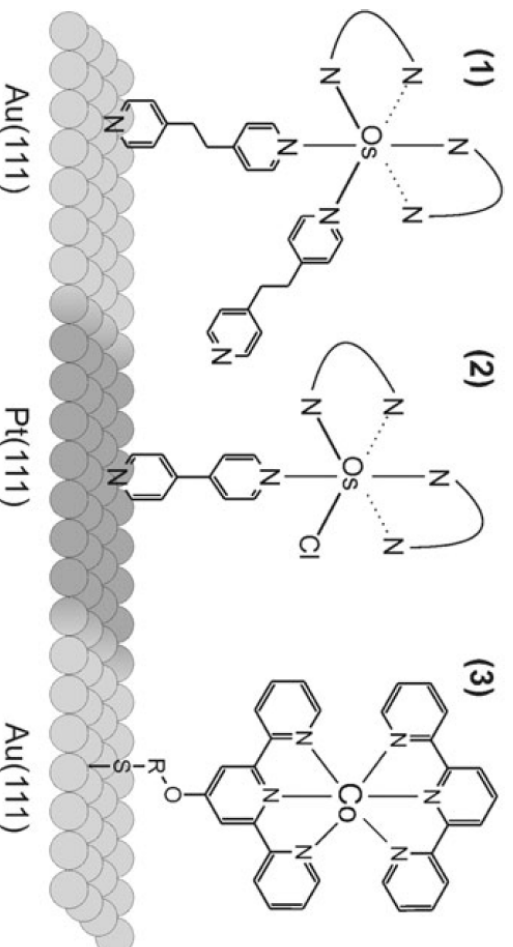
99

	$\beta, \text{ \AA}^{-1}$	$\beta, \text{ per C}$
	0.79	$\sim 1$
	0.27	0.34
	0.27	

**Table 5.2** Commonly reported  $\beta$  values for different kind spacers [Adams et al., J. Phys. Chem B. 2003].

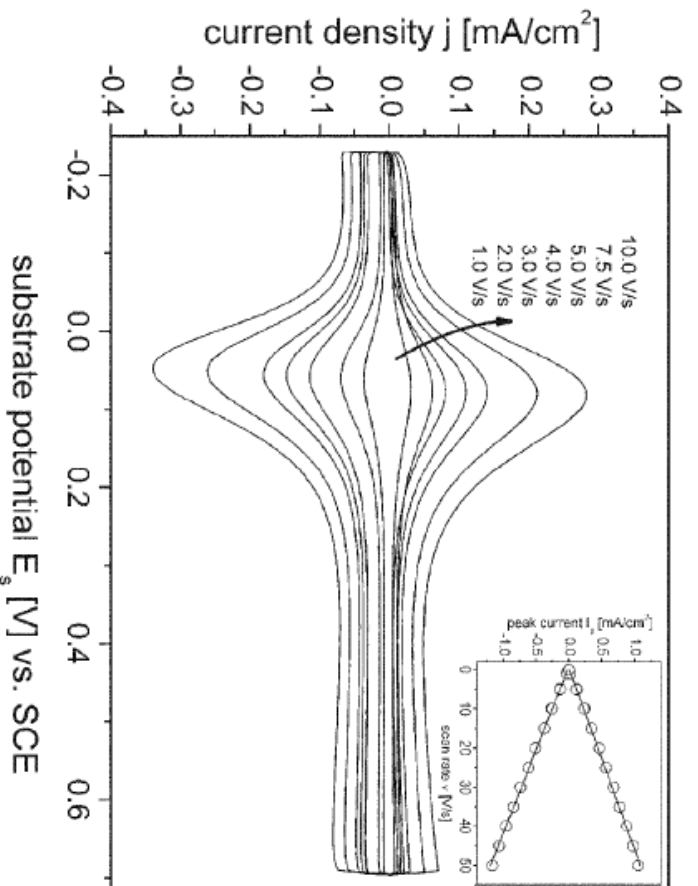
### 5.3 SAM as molecular linkers

- Redox species assembled in organised 2D layers at electrode surfaces.
- Mass transport is not relevant.
- Current responses proportional to *surface excess*  $\Gamma$  ( $\text{mol cm}^{-2}$ ) of the redox species.



**Fig. 5.8** Redox species confined to electrode surfaces via self-assembly [Albrecht et al. Faraday Disc. 2006].

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**Fig. 5.9** Cyclic voltammograms of the complex 3 (figure 5.8) assembled at Au surfaces at various scan rate. The system shows a reversible response [Albrecht et al. Faraday Disc. 2006].

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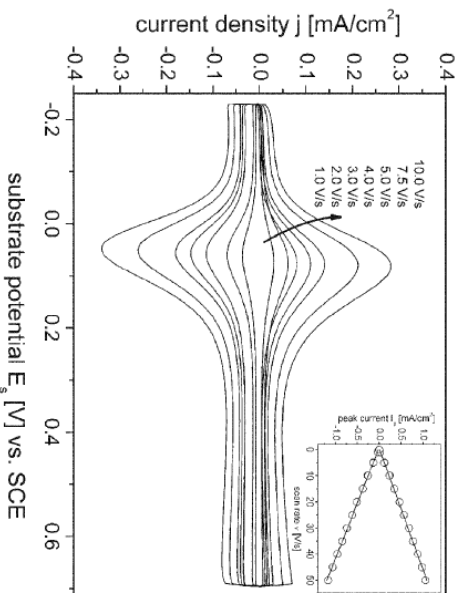
## Cyclic voltammetry of reversible surface confined redox species

$$i = \frac{n^2 F^2}{RT} \nu A \frac{\Gamma_R^* \exp \left[ \frac{(nF/RT)(E - E^{\phi'})}{RT} \right]}{\left( 1 + \exp \left[ \frac{(nF/RT)(E - E^{\phi'})}{RT} \right] \right)^2} \quad \text{eqn. 5.10}$$

$$i_{\text{peak}} = \frac{n^2 F^2}{4RT} \nu A \Gamma_R^* \quad \text{eqn. 5.11}$$

$$E_{\text{peak,a}} = E_{\text{peak,c}} = E^{\phi'}$$

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**Fig. 5.9** Cyclic voltammograms of the complex 3 (figure 5.8) assembled at Au surfaces at various scan rate. The system shows a reversible response [Albrecht et al. Faraday Disc. 2006].

➤ Peak current ( $i_{\text{peak}}$ ) is directly proportional to the scan rate ( $\nu$ ).

➤ The area under the peak is given by  $nFA\Gamma_R^*$

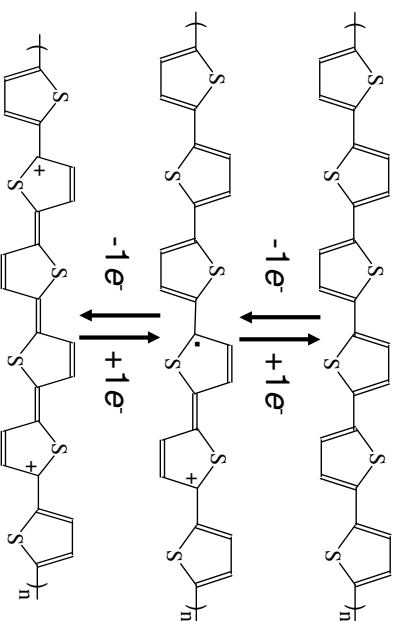
➤  $\Delta E_{1/2} = 90.6/n \text{ mV}$  (25 °C)

➤ Quasi-reversible systems: peak potentials separate from each other [Bard 2000].

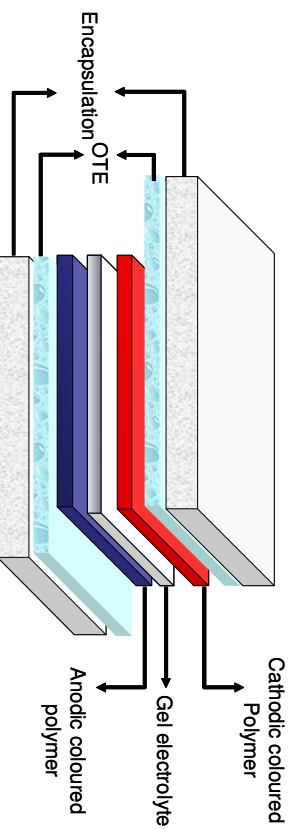
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## 5.4 Redox active polymers

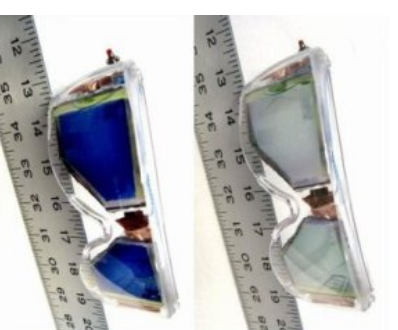
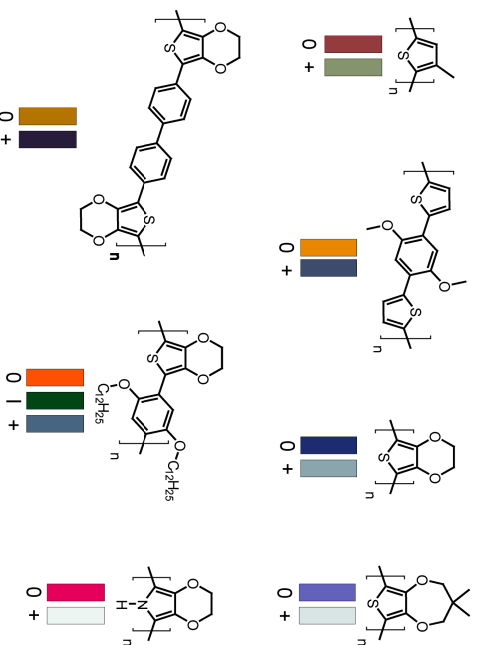
- Flexible and low-cost electronics
- Smart windows and electrochromic devices
- Biocompatible actuators
- Solar cells and light emitting devices



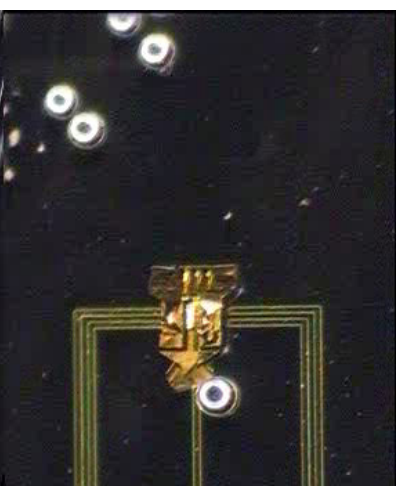
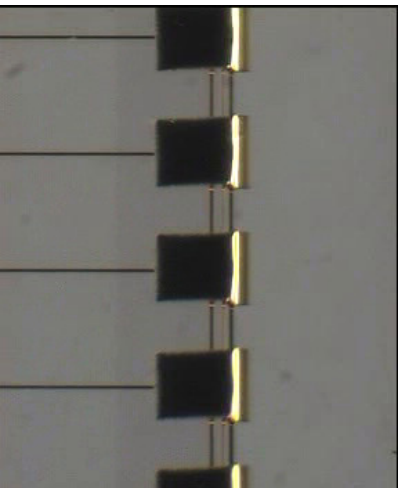
105



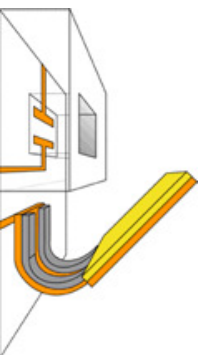
**Fig. 5.12** Schematic diagram of a polymer-based electrochromic window.  
[Argun, Adv. Mater. 2003].



## Actuators and artificial muscles.



Micro-robot 0.7 mm lifting object of 0.1 mm.



Micro-chamber 100 mm × 100 mm × 20 mm.

Videos downloaded from [www.micromuscle.com](http://www.micromuscle.com)

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## Summary

- ✓ Tuning redox activity of electrodes via self-assembling molecules and conducting polymers
- ✓ Tunnelling probability (electron transfer) decreases exponentially with distance
- ✓ Surface confined species: Bell-shape current vs potential responses and peak current is linearly dependent of the scan rate

$$i_{\text{peak}} = \frac{n^2 F^2}{4RT} v A \Gamma^*$$

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# Giants of the day



Alan Heeger  
American Physicist  
1936 -



Alan MacDiarmid  
New Zealander Chemist  
1927 - 2007



Hideki Shirakawa  
Japanese Chemist  
1936 -