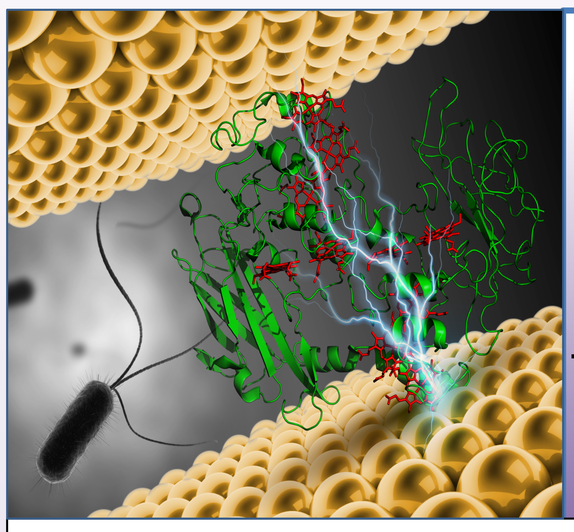

Direct evidence for heme-assisted solid-state electronic conduction in multi-heme *c*-type cytochromes

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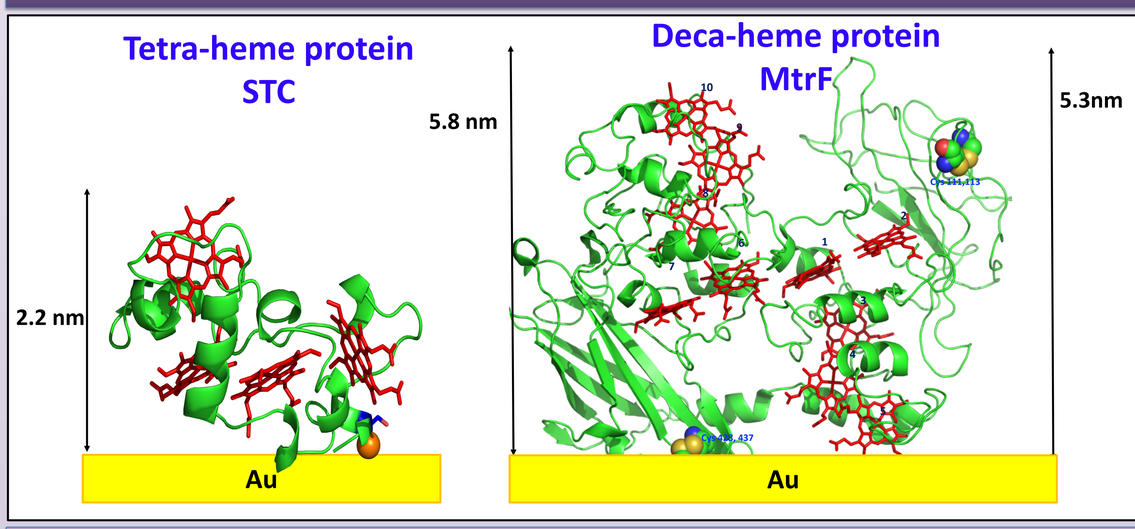
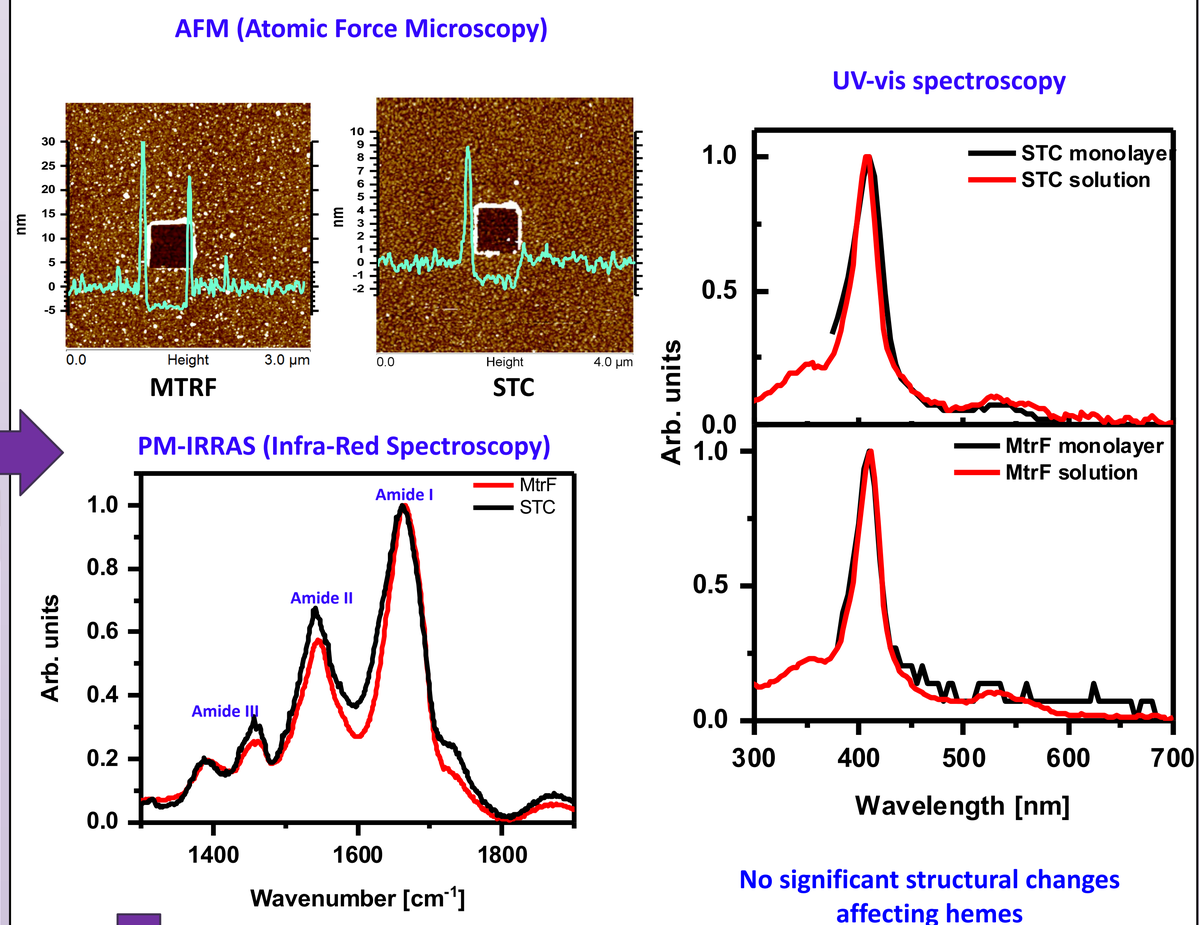
Multi-heme cytochrome C (Cyt*C*) proteins are key for transferring electrons out of bacterial cells, to enable intracellular oxidation to proceed in the absence of O_2. In these proteins most of the hemes are arranged in a linear array, suggesting a facile path for electronic conduction. To test this, we studied *solvent-free electron transport* across two multi-heme Cyt*C*-type proteins: MtrF (deca-heme Cyt*C*) and STC (tetra-heme Cyt*C*). Transport is measured across protein monolayers *in a solid state configuration* between Au electrodes. Both proteins showed conductances ~1000× higher than across single heme or heme-free proteins, but similar to monolayers of conjugated organics. Conduction is found to be temperature-independent (320–80 K), even across the large deca-heme, suggesting tunneling as the transport mechanism. This mechanism is consistent with *I–V* curves modelling, results of which could be interpreted by having *protein-electrode coupling* as rate-limiting, rather than transport within the proteins.

Scheme of Au bound protein using 3D structures

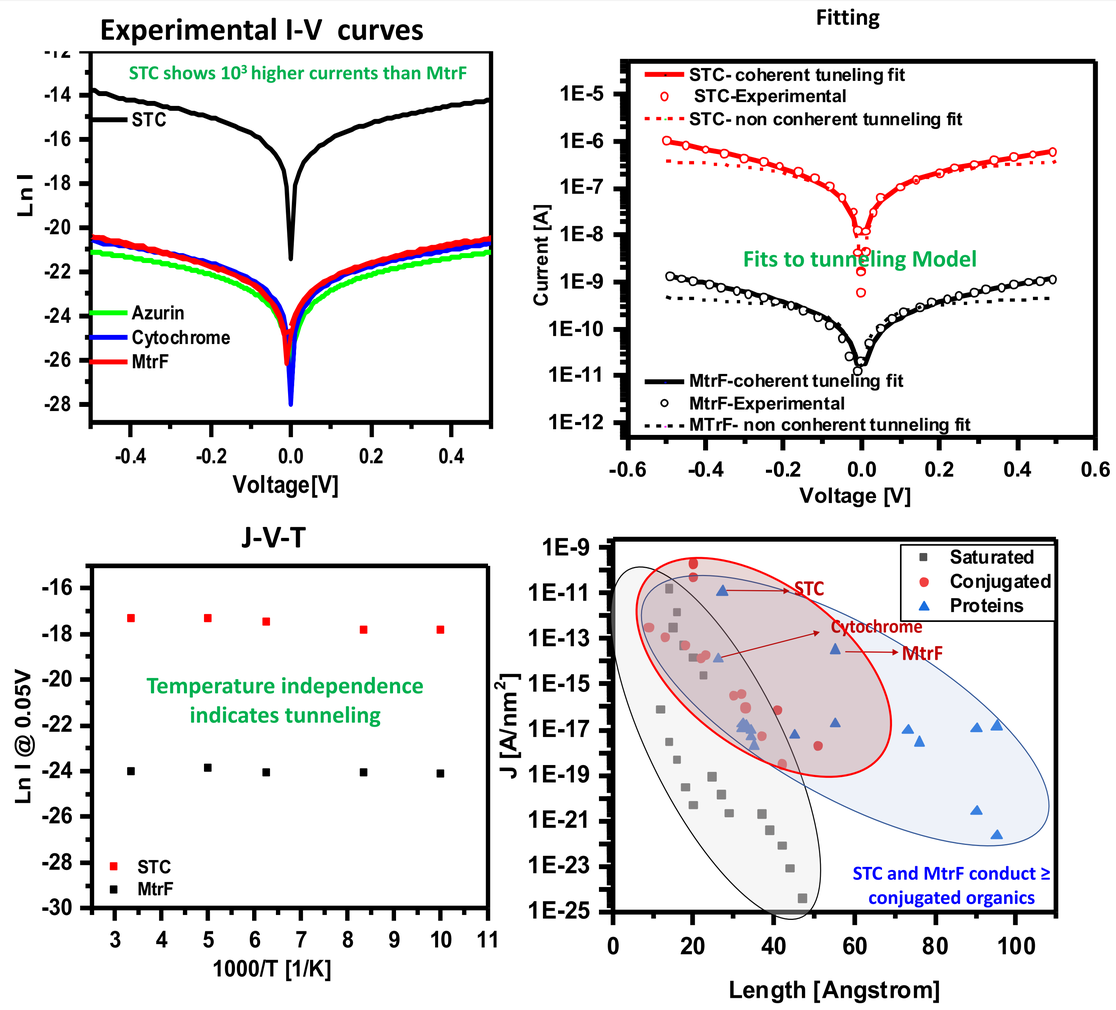


Characterisation of monolayers

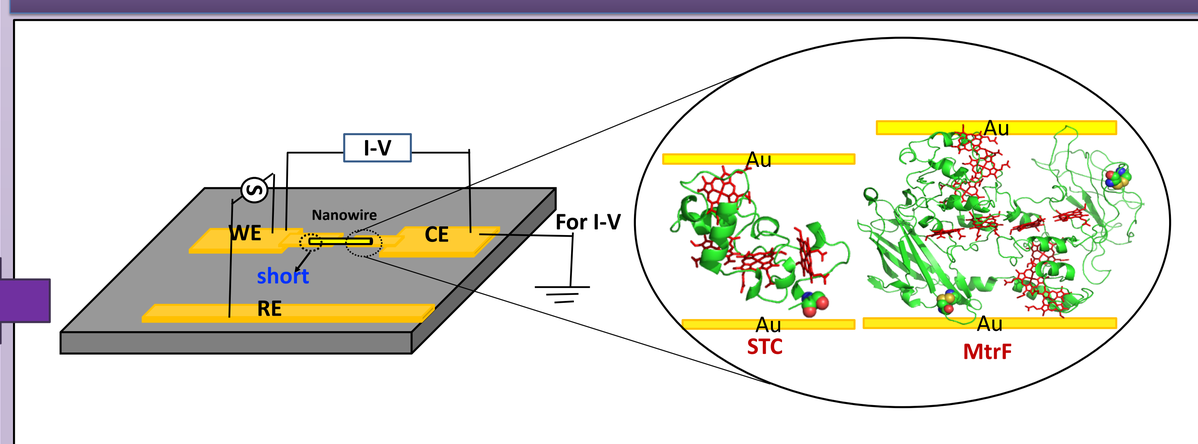


No significant structural changes affecting hemes

Current -voltage (Au-proteins-Au) measurements



Device Configuration



- Au nanowire deposition by electrophoresis (from solution with AC bias between WE and RE).
- I-V measurements are done between WE and CE in dry state in 10^{-5} bar pressure.

Conclusions

- **Multi-heme proteins, MtrF and STC, are markedly better solid-state (dry) electronic conductors than non- or mono-heme proteins in MONOLAYERS , and similar to, or better than conjugated organic molecules.**
- **The electron transport process, being temperature-independent and the good fits of the experimental I-V curves with a coherent tunneling model, support that *transport is via tunneling, even for the ~ 5 nm thick MtrF monolayer!***
- **Possibly tunneling is from/to the electrodes to/from one of the hemes nearest to the electrodes; if so, then intra-protein conduction is so fast that it leaves no footprint in the experimental I-V and G-V curves.**
- **No evidence for structural changes in the proteins (in the monolayer) could be resolved.**
- IETSpectra fit PM-IRRAS ones, and prove amino acid and heme presence between the contacts.

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