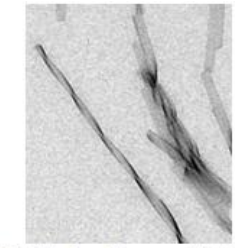
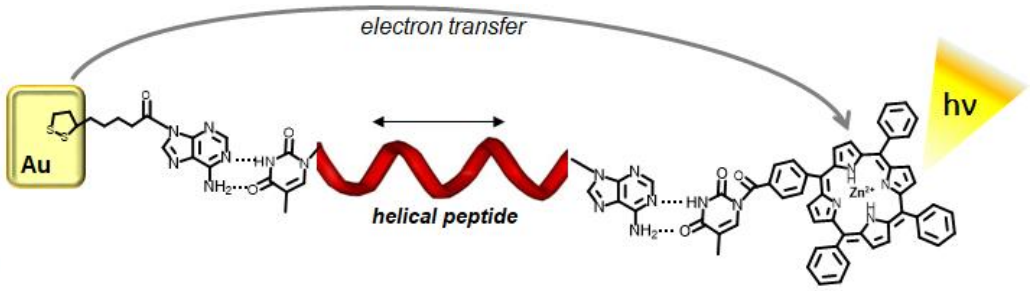
Photocurrent generation in a supramolecular DNA-inspired peptide nanowire

In Nature, electron transfer (ET) is performed by means of biomolecules. Helical peptides are known to effectively mediate ET, acting as biomolecular wires, but they offer little stability outside their natural environment. Natural peptides based on sterically hindered, non-coded α-amino acids are biopolymers that possess - even when short - well-defined helical structures, remarkably stable under extreme environmental conditions. In this presentation, we will see how a bioinspired approach based on nucleobase pairing allows the helical peptides to self-organize into molecular wires. First, we synthesized a helical undecapeptide analog of the natural peptide trichogin GA IV functionalized with thymine and adenine at its N- and C-termini, respectively. Through thymine-adenine hydrogen bonds, we assembled the biodevice onto a gold electrode, capping it with a Porphyrin(Zn)-Adenine, also through hydrogen bonding. Under illumination, the peptide-based supramolecular system efficiently generates current [1] while remaining very stable over time, also in contact with a solution. We can modulate the photocurrent efficiency by inducing a reversible, pH-controlled 3_{10}-helix to α-helix conversion: the pH-induced conformational change can act on the electron transfer, by changing the molecular dipole moment [2,3]. The biomolecular devices were



TEM of self-assembled peptide wire



characterized by electrochemical and spectroscopic techniques, and were able to generate current under illumination, with an efficiency that is the highest recorded so far with biomolecular systems.

[1] E. Gatto, S. Kubitzky, M. Schriever, S. Cesaroni, C. Mazzuca, G. Marafon, M. Venanzi, M. De Zotti, *Angew. Chem. Int. Ed*. **2019**, *58*, 7308.
[2] S. Kubitzky, M. Venanzi, B. Biondi, R. Lettieri, M. De Zotti, E. Gatto, *Chem. Eur. J.* **2021**, *27*, 2810.
[3] S. Kubitzky, R. Lettieri, E. Passaretti, M. Venanzi, M. De Zotti, C. Mazzuca, E. Placidi, E. Gatto *Adv. Mater. Interfaces* **2025**, *12*, 2400418.