

## Porphyrins in electronics

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Porphyrins are highly conjugated, intense colored and the core of key biomolecules “hemoglobin and chlorophyll”. Biological systems use porphyrins and metalloporphyrins as catalysts, small molecule transporters, electrical conduits and energy transducers in photosynthesis, hence are an obvious class of molecules to investigate for molecular electronic functions. As a class of molecule, they are robust; possess distinctive reversible oxidation and reduction chemistry. As synthetic porphyrin chemistry is well developed and molecular orbital models accurately predict the electronic consequences of appending organic substituents and binding metal ions. Electronic properties of porphyrins can be tuned by chelation of a metal ion and substitution on the macrocycle that potentiates their use as wires, switches, transistors, junctions, and photodiodes. There are two notable early examples of supramolecular devices based on porphyrins, one as photo-gated ion conductors and another as memory device. Here, we have demonstrated molecular resonance tunneling diode and molecular rectifier based on porphyrin molecules. Resonance tunneling diode is constructed on a  $\sigma$ - $\pi$ - $\sigma$  molecular architecture, with a ‘quantum well (a  $\pi$  conjugated molecule “Porphyrin”)’ surrounded by tunnel barriers ( $\sigma$  alkyl chains), electro-grafted on H-terminated Si. These devices exhibited reversible, stable (up to 8 h of voltage scanning) and room temperature NDR (Negative Differential Resistance) effects. Molecular rectifier with donor-spacer-acceptor (D-s-A) structure, electro-grafted on H-terminated Si behaves as a diode. These devices showed RR (Rectification Ratio) up to  $10^7$  in reverse bias as a result of alignment of the LUMO levels of the molecules with the Fermi-levels of the electrodes.

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## Fluorescent carbon nanotube biosensors for probing intracellular kinase hyperactivation in human cancer

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Cyclin-dependent kinases (CDK/Cyclins) play a central role in coordinating cell growth and division and are frequently deregulated in cancer, thereby constituting proliferation biomarkers and attractive pharmacological targets. However, probing and quantifying the hyperactivity of these kinases remains challenging, and there are no technologies available to monitor their activity in living cells in a non-invasive fashion. To this aim, we have developed a family of fluorescent biosensors, known as CDKACT, through conjugation of environmentally-sensitive probes to synthetic peptides which are specifically recognized by CDK/Cyclins and undergo fluorescent enhancement upon phosphorylation. We have further conjugated these peptide biosensors at the surface of multiwall carbon nanotubes to obtain self-cell-penetrating sensors of intracellular kinase activity. We show that these carbon nanotube peptide conjugates report on CDK/Cyclin activities in a sensitive and robust fashion *in vitro*. Moreover, these nanobiosensors penetrate readily into living cells and enable detection and quantification of the intracellular activities of these kinases by fluorescence imaging. This new generation of hybrid carbon nanotube peptide biosensors constitute attractive tools for cancer diagnostics and for evaluating response to therapeutics. They are particularly well suited for molecular imaging and are currently being implemented to monitor CDK/Cyclin hyperactivity associated with cancer progression and inhibition in mouse cancer models.

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