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Inspired by Photosynthesis

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The inspiration from electronic and ionic phenomena in green plants and other photosynthetic organisms have been one of my guiding lights over the last 40 years. I will revisit three recent results in this talk. It all starts in Italy: Alessandro Volta and Luigi Galvani created concepts and theories for the electrical aspects of living matter. Their work started out in the electrical phenomena of frog muscles, metals and charcoal, to initiate the field of electrochemistry, later transforming into bioelectrochemistry, and soon venturing on to new ways of interacting between the world of digital computing and biological organisms.

The major biological system for energy conversion, photosynthesis, has accumulated the fossil fuels still dominant in energy supply, which must be substituted by renewable energies from solar radiation. As the second level quantum technology is now evolving, in physics and computer science, it is natural to ask whether also living systems has somehow utilized coherence phenomena in biological processes. A most controversial topic in the study of photosynthesis is the possible role of quantum coherence in generating the very efficient charge separation in early phases of the transition from excited states in molecular chromophores, to formation of proton gradients over biomembranes, with later conversion to ATP for bioenergetics in complex biochemical networks.

With the ongoing development of organic photovoltaic materials and devices, similar suggestions of quantum coherence in the transition from excited states to (separated) charge pairs are proposed. We have presented experimental evidence for the presence of vibronic coherence in studies of ternary donor/acceptor blends, using optical transient methods and nonlinear 2-dimensional photocurrent spectroscopy [1]. The interpretation of these phenomena as due to coherence, assisted by molecular vibrations. visible in Raman spectroscopy, argues that also in less organized materials, such physics may be relevant.

The dynamic disorder of green photosynthetic machinery is in no way a hindrance for the operation of the very high efficiency charge separation; indeed, it is suggested that the dynamic molecular geometry of chromophore/protein assemblies contribute to the stabilization of photogenerated charges. As disorder is the most obvious structural property of the donor/acceptor blends of organic molecules and polymers, used in organic photovoltaic devices and now with the power conversion efficiency record of $\approx 18\%$, it is of general interest to understand how far this efficiency can be taken.

We know the Shockley-Queisser thermodynamic limits for photovoltaic energy conversion using semiconductors. These limits are based on equilibrium thermodynamics, and over the years the classification of OPV systems as equilibrium systems have become orthodoxy [2]. Charge carriers generated by photoexcitation will have a very high initial effective mobility, but during the transport by hopping in these disordered systems, the effective mobility rapidly is reduced. As demonstrated in a few systems, the photogenerated charge carriers are not at thermal equilibrium when exiting at contacts^[3]. Therefore, OPV devices are hot carrier photovoltaic devices, and the thermodynamic equilibrium analysis does not fully apply. The implications may be that the limits for excitonic OPV devices are different than for fully equilibrated semiconductors, based on crystalline materials with extensive delocalisation of charge carriers. Another aspect of non-equilibrium is the geometry of OPV materials, as prepared from solvents, that are not in thermodynamic equilibrium, but rather kinetically trapped.

Storage of electrical energy in scalable materials is the most urgent technology need for renewable electricity. As a sequel to the very rapid charge separation in green plant thylakoids, the stabilized charges are transported by diffusion of quinone molecules across a biomembrane. The choice of a quinone species---which can be found as early as with *Archea* species- is a common theme in living systems, where a two electron/two proton process converts an oxidized quinone to a reduced quinone. The small molecule quinones are synthesized by the biological organisms, starting with amino acid precursors. Such precursors are also used in the formation of lignin, the biopolymer present in green plants, and only outnumbered by cellulose in biomass. By oxidation of lignin, quinone species can be generated, and can be used in organic cathodes for charge storage. The alternatives of quinones in pure form, or integrated in biopolymers,

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from different sources are highlighted in our development of wooden electrodes for green batteries/supercapabatteries[4].

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