Probing the interaction of nanotubes and photosynthetic complexes

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Application of carbon nanotubes (CNTs) in plant biotechnology and agriculture brought to light an increasing amount of new findings, revealing the potential of CNTs to promote plant growth and production, or to control the delivery of genetic material, fertilizers or pesticides to plant tissues [1,2]. It was also suggested that part of the energy absorbed by CNTs may be transferred to photosynthetic reactions and increase photosynthetic activity *in vitro* and *in situ* [3]. This experimental clue promoted the possibility to exploit the high light-capturing efficiency and broad absorbance of CNTs to enhance plant light harvesting capacity. However, the few studies focused on the CNT interplay with photosynthetic complexes (PSCs) provide quite ambiguous results. Beside the energy allocation from the CNTs to the PSCs, an excitation energy or charge transfer from the photosynthetic complexes forward the nanotubes seems equally possible [4,5]. Importantly, the studies dealing with CNTs/PSC interactions exploit different biological specimen, including isolated chlorophyll molecules, reaction centers, thylakoid membranes (TMs) or light-harvesting complexes (LHCs), and various experimental conditions that might also contribute to the observed CNT mode of action.

Here we aimed to gain insights into the electro-optical interactions of CNTs with light-dependent photosynthetic reactions using isolated PSCs and supramolecular assemblies with different level of complexity (Fig. 1) under controlled experimental conditions. The TMs present the most complex approximation of the photosynthetic machinery involved in light energy harvesting and conversion, and contain all cofactors involved in the electron transport chain and the complex responsible for ATP synthesis (Fig. 1b). BBY preparations are oxygen evolving, Photosystem II-enriched membrane fragments, in which the luminal side of the membranes is exposed toward the solution; they lack PSI and ATP-synthase (Fig. 1c). LHCII, the peripheral light-harvesting complex of PSII, was selected as a simple pigment-protein assembly not able to perform charge separation (Fig. 1d). The biological specimen was enriched with different concentrations of well-dispersed single-walled CNTs and the biohybrid systems were analyzed by steady-state and time-resolved chlorophyll fluorescence spectroscopy. Attention was payed to exclude possible osmotic effects on the aggregation degree of the complexes and to evaluate changes in optical properties of the systems, which may affect the absorption and fluorescence features of the CNTs/PSCs assemblies. This experimental set up allowed us to analyze and compare energy and electron fluxes in biohybrid systems hosting PSCs with different functional role in the photochemical reactions of photosynthesis. CNTs were found to alter the excitation energy pathways already at the antenna level. There were evidences for accelerated excitation decay in the photosynthetic structures in all studded model systems. The possible biochemical interactions and photophysical processes involved will be discussed.

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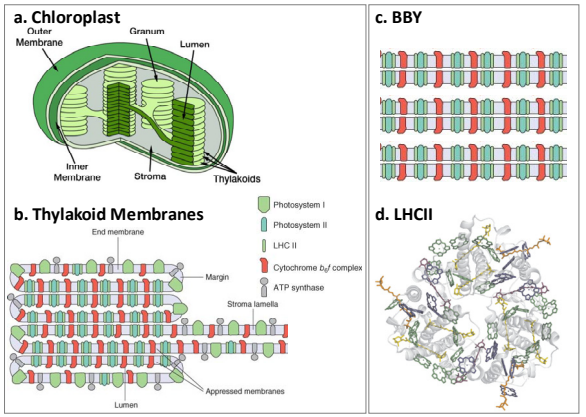

Figure 1. ***(a.)*** Schematic presentation of chloroplast structure with granal (grana stacks) and stromal thylakoid membranes [6]; ***(b.)*** A cross section of a thylakoid showing the different membrane regions including the appressed membranes in the grana stacks (only PSII, LHCII and cyt. b6f complex), and end and stromal membranes (containing all photosynthetic complexes and ATP-synthase) [7]; ***(c.)*** A cross section of the so-called BBY preparations, PSII-enriched membrane fragments; ***(d.)*** 3D-structure of LHCII-trimer with associated pigments [8].