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A Photosynthetic Reaction Center Covalently Bound to Carbon Nanotubes**

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The photosystem I (PS I) reaction center is a chlorophyll protein complex located in thylakoid membranes of chloroplasts and cyanobacteria. PS I mediates a light-induced electron transfer through a serial of redox reactions.[1] It is intriguing to incorporate the PS I into optoelectronic circuits, since the PS I exhibits outstanding optoelectronic properties found only in the photosynthetic systems. The quantum yield for absorbing a photon within the whole complex is determined to be close to 100 %, while the energy yield for the process is approximately 58 %.[1] The nanoscale dimension and the generation of 1 V photovoltage further makes the PS I reaction center a promising unit for applications in molecular optoelectronics.[2–6] Utilizing a unique cysteine (Cys) mutation at the end of PS I, we demonstrate a four-step chemical procedure based on carbodiimide chemistry for covalent binding of PS I proteins to carbon nanotubes (CNTs).[7] The method allows studying hybrid nanosystems for the construction of optoelectronic devices based on PSI-CNTs heterostructures. Three variations in the design of PSI-CNT hybrid structures are presented which allow exploiting the potential of PS I as an integrated part of CNT nanodevice for optoelectronic applications.

Recently, we have demonstrated the possibility to covalently bind PS I directly to gold surfaces[5] and indirectly via a small linker molecule to GaAs surfaces.[6] To this end, amino acids in the extra membrane loops of the PS I facing the cytoplasmic side of the bacterial membrane (oxidizing side) were mutated to cysteines (Cys) enabling the formation of covalent bonds with a metal surface or a chemically functionalized GaAs surface. The Cys located at extra membranal loops of the protein do not have steric hindrance, when placed on a solid surface e.g. of a gold electrode or CNTs as shown here. The mutations D235C/Y634C were selected near the special chlorophyll pair P700 to allow close proximity between the reaction center and the CNTs.[5] As depicted by white arrows in Figure 1, here we utilize a PS I with two mutants on the oxidizing side of the PS I. This single sided mutant ensures a high outcome of our chemical self-assembly procedure. For a variation of our chemical scheme we also use bipolar (BM) mutants, where the mutations are located at both the oxidizing (white arrows) and the reducing side of the PS I (gray arrow). Our self-assembly approach facilitates efficient electronic junctions and avoids disturbance in the function of the reaction center. The covalent attachment of the PS I through the Cys further ensures the structural stability of the self-assembled, oriented PS I. As demonstrated recently,[5,6] a dry oriented monolayer of PS I assembled on gold electrodes and GaAs surfaces exhibits charge transfer between PS I and the solid state surface.

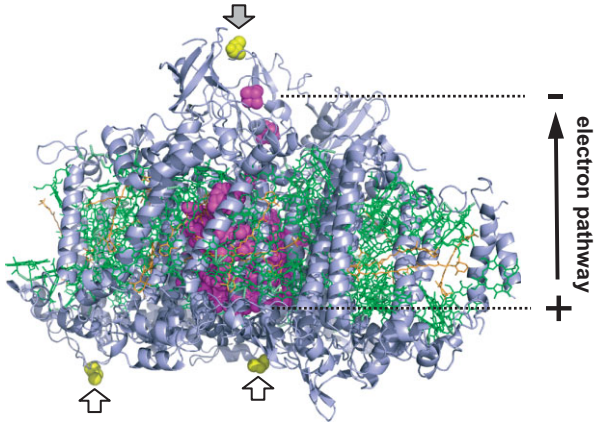

Figure 1. Molecular structure image of the photosynthetic reaction center I (PS I) based upon crystallographic data. PS I is composed of polypeptide chains (gray) in which chlorophyll (green) and carotenoids (orange) are imbedded. The black arrow schematically depicts the light induced charge separation across the PS I. The chromophores which mediate the electron transfer are represented by the space fill model (cyano) [1]. The PS I covalently binds to maleimide modified carbon nanotubes through Cys mutations along the polypeptide backbone (arrows and space fill model, yellow). See text for details.

In this work, we extend the above chemical scheme in order to covalently attach PS I proteins to CNTs. The hybrid systems are characterized by atomic force microscopy and

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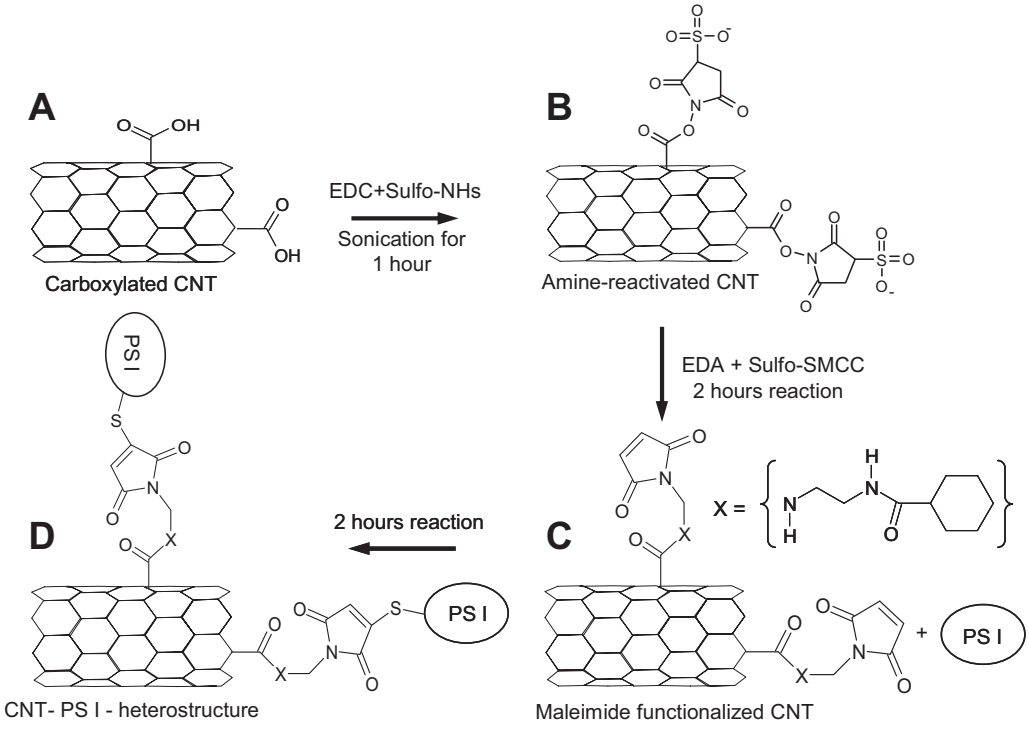
UV-VIS spectroscopy, indicating a high degree of conjugation between the PS I and the CNTs.

Generally, the PS I complex consists of twelve polypeptides, to which ninety-six light-harvesting chlorophyll and twenty-two carotenoid pigment molecules are bound.[1] The PS I protein has a cylindrical shape with a diameter of about 15 nm and a height of 9 nm. Following photo excitation, an electron is transferred along the electron transfer pathway within the protein complex (black arrow in Fig. 1). The initial optical excitation of the special pair of chlorophyll a (P700) is followed by an electron transfer to a monomeric chlorophyll a (Chl) within one picosecond. The excited electron relaxes via two intermediate phylloquinones (PQ) to three [4Fe-4S] iron sulfur centers (FeS) within approximately 0.2 μs. The final acceptors are located about 6 nm away from the oxidized P700 (Fig. 1). Intriguing for optoelectronic applications, the photoexcited state of the PS I provides a surface photovoltage of up to 1 V, which translates into an electric field of about 1 V/6 nm = 1.6×10^8 V m^{-1}.[5] Of special interest is the coupling between PS I and carbon nanotubes (CNTs), which have emerged as promising building blocks of nanoscale electronic devices and sensors.[7–15] The optical properties of single-wall CNTs further suggest potential applications in nanoscale optoelectronic circuits.[16–19] The photoconductivity of CNTs has been measured for ensembles of CNTs[19] and for individual single-wall CNTs[16,20], demonstrating the application of CNTs as photodetectors and infrared-light emitters.[21,22] The length of CNTs of up to several micrometers further qualify CNTs as mesoscopic electrodes for nanoscale electronic components such as molecules[23] and nanocrystals.[24] The functionalization of carbon nanotubes by chemical modifications holds interesting prospects in various fields such as nucleic acid sensing[25] and the fabrication of hybrid bioorganic nanosystems.[26–31] In particular, it has been demonstrated how to covalently bind single-wall CNTs to DNA[22,27], nanocrystals to multi-wall CNTs[28,29], and multi-wall CNTs to the end of an AFM tip.[32]

Scheme 1 illustrates the procedure used in the synthesis of the hybrid systems involving carbodiimide chemistry. The procedure for covalent binding of PS I to the carboxyl groups on the surface of the CNTs can be described in four steps. In step A, CNTs (Rice Company Inc) were purified and functionalized with carboxyl groups by refluxing in 3 M HNO_3 for 10 hours. Several filtration cycles through a 0.1-micrometer PTFE-filter in a medium containing the surfactant Triton-X, 0.2 % (Sigma-Aldrich) enabled an additional removal of small particles. A 2 ml suspension of CNTs in 0.2 % Triton X was dialyzed in bags (molecular cut off of 8000 Daltons, Spectra/por Biotech RC membranes).

The suspension was stirred and washed for 24 hours with deionized water 0.2 % Triton X and replaced every couple of hours by a fresh solvent. Aliquots of 0.5 mg of carboxylated CNTs were suspended in 2 ml deionized water 0.2 % Triton-X and sonicated briefly (Scheme 1A). In step B, amine reactive NHS-esters of the CNTs bound carboxylic acids are achieved by sonication of the CNTs suspension in the presence of 0.1 M MES buffer PH-4.5 0.2 % Triton-X, 5 mM of 1-ethyl-3-(3-dimethyl amino-propyl) carbodiimide (EDC, Pierce) and 5 mM



Scheme 1. Schematic representation of the chemical procedure forming heterostructures of carbon nanotubes (CNTs) and PS I (pictures are not to scale). See text for details.

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Sulfo-NHS (Pierce) for one hour at room temperature (Scheme 1B). In step C, we covalently modified the amine reactive NHS-ester CNTs with Sulfo-SMCC, which contains a sulfhydryl reactive maleimide group. To this end, 5 mM of ethylenediamine (EDA, Pierce) were first reacted with 5 mM of Sulfo-SMCC (Pierce) in 0.1 M PBS buffer pH 7.2. Then the amine reactive NHS-esters CNTs were added to the solution, and in turn the pH was adjusted to pH 7.2 with constant stirring for two hours. The sulfo-SMCC activated CNTs were washed from the excess reagents by several filtrations and centrifugation steps. The maleimide modified CNTs were then suspended in 0.2 % Triton-X, 0.1 M PBS buffer pH 7.2 and sonicated briefly resulting in a clear blackish transparent supernatant (Scheme 1C). In step D, the CNT-PS I hybrid systems were fabricated by directly reacting the Cys of a single sided PS I mutant (which has two Cys mutations at the oxidizing side of the PS I, see Fig. 1) with the maleimide group of the sulfo-SMCC activated CNTs. Prereduction of the thiol Cys in PS I was done by incubating aliquots of 1.6 mg chlorophyll/ml PS I in the presence of 2 mM dithiothreitol (Sigma-Aldrich). The excess reagent was removed by three passages over G-25 sephadex column (Sigma-Aldrich) equilibrated with 20 mM tricine, pH 7.5, 0.05 % n-dodecyl β-D-maltoside (Sigma-Aldrich). A 0.5 ml aliquot of the activated suspension of PS I was added to the maleimide modified CNTs and stirred for 2 hours at room temperature. Following incubation, the reaction mixture was washed by several centrifugation cycles in 0.1 M PBS buffer, pH 7.2, 0.2 % Triton-X to remove unbound PS I. Finally, the reaction mixture was suspended in 2 ml of the buffer solution (Scheme 1D). To evaluate the degree of hybridization between modified CNTs and PS I, a drop of the supernatant solution was placed onto a silanized silicon surface, and incubated for two hours. The samples were washed briefly with deionized water and dried under nitrogen.

Figure 2 shows an atomic force micrograph (AFM) images of the CNT-PS I hybrid systems on a silanized surface. The images exhibit a large number of spherical particles attached to the surface of the CNTs. The height analysis of the AFM images (lower insets) indicates a diameter of about 10–20 nm for the spherical particles, in agreement with the actual diameter of the PS I, which suggests that the spherical particles are the PS I proteins. The diameter of the CNTs is in the range between 1 and 2 nm (data not shown). Figure 2A and B depict hybrid systems made out of the PS I and single-wall CNTs, while Figure 2C displays a ring-shaped hybrid system formed by PS I and a multi-wall CNT. Following the chemical procedure as in Scheme 1, we found linear and ring-shaped hybrid systems for both single-wall and multi-wall CNTs. The ring formation is attributed to a tube-tube van der Waals adhesion during the purification step (Scheme 1A), as recently discussed.[33] The PS I particles are detected at varying densities along the sidewalls of the CNTs. In some cases higher densities of PS I are observed at the ends of the CNTs (Figure 2A). The latter experimental result agrees well with the fact that the carboxylation process is most effective at the ends of the CNTs.[34] It was suggested that acid oxidation of CNTs generates defects more efficiently at the loosely bound carbon atoms at the tip of the CNTs rather than at the side walls of the CNTs. The topological variation in the binding of the PS I observed here is not detected in samples, where the PS I is just bound via Van der Waals or dipole-dipole interactions.[35]

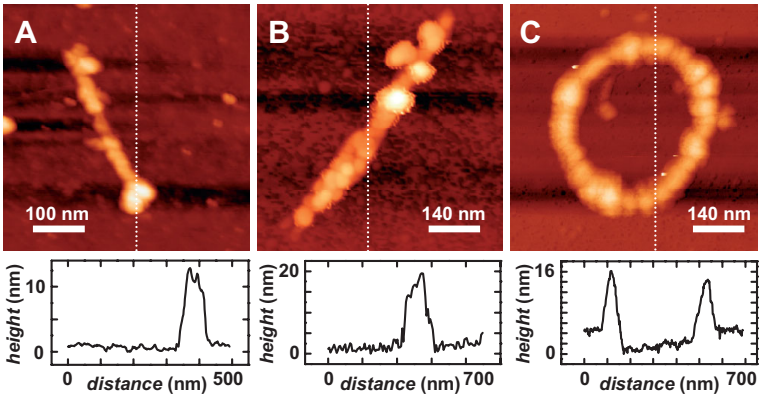

Figure 2. Atomic force micrographs of PS I bound to single-wall CNTs (A and B) and to multi-wall CNTs (C). The images show a large number of PS I with a diameter of about 10–20 nm bound to the side-walls and the tips of CNTs. The insets depict single trace lines along the dashed curves in the main figures.

Figure 3 illustrates the absorbance spectra of (A) the PS I suspended in buffer solution and the absorbance of maleimide modified CNTs (B) before and (C) after the reaction with PS I. Chlorophyll absorbance maxima are at ~ 440 nm and 680 nm, and the carotenoids contribute to a shoulder at 500 nm.[1] As can be seen in Figure 3C, the hybrid systems exhibit absorbance features which correspond to the PS I (open triangles) and the CNTs (closed triangles). The solution containing the hybrid systems was filtered several times to remove unbound PS I. Hereby, the presence of PS I absorption resonances in the hybrid systems is a further indication for the binding of PS I to the CNTs. Figure 3D highlights the spectra of the PS I, the CNTs, and the hybrid systems at a wavelength of $\lambda \sim 680$ nm. To first approximation the spectrum of the hybrid systems is a superposition of the absorbance resonances of the CNTs (closed triangles) and the PS I (open triangle). We interpret the observation such that the photosynthetic complexes are preserved during the chemical coupling. It is important to note, that the spectra in Figure 3 were normalized after a Rayleigh background $a\,\lambda^{-4}$ was subtracted. Hereby, the absolute and the relative heights of the absorption resonances in Figure 3A–C can not be compared to each other. Generally, the absorbance features of the CNTs can be explained by the one-dimensional subband energies of the semiconducting CNTs within the ensemble of CNTs and the functionalized chemical groups of the CNTs.[36] For $\lambda > 700$ nm only the CNTs are assumed to absorb photons, which can be seen in the spectra of the unbound CNTs and the CNTs-PS I hybrids.

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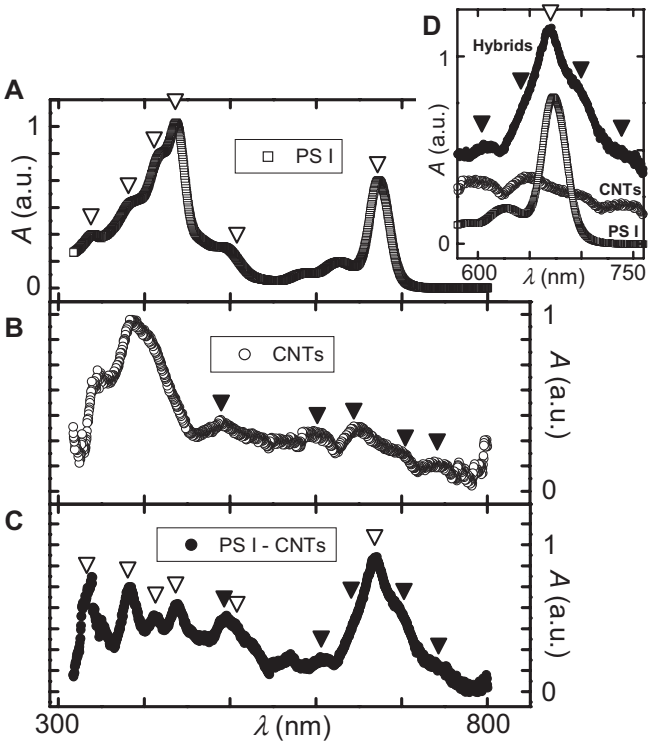

Figure 3. Normalized absorbance of A) the PS I (open squares), B) the CNTs (open circles), and C) the CNTs-PS I hybrid (circles). D) Close-up of all spectra at a wavelength of about 680 nm. The data of the hybrid systems (top) show features which originate from both the PS I (open triangle) and the CNTs (black triangles). Data are off-set for clarity. See text for details.

By modification to step D of the chemical procedure, we were able to construct a cross junction between two CNTs connected via the PS I. To this end, single-wall CNTs are first functionalized with maleimide according to step A, B, and C. Then, a bipolar mutant (BM) of PS I, which has a Cys mutation at both the reducing and oxidizing side of the reaction centre, was introduced to the modified CNTs. The solution was incubated for two hours in the presence of 0.1 M PBS buffer pH 7.2, 0.2 % Triton-X. Following the incubation, the excess of reagents and unbound PS I were washed by several centrifugation cycles with 0.1 M PBS buffer (pH 7.2, 0.2 % Triton-X) and the CNTs were suspended in 2 ml of the buffer solution. A second batch of maleimide modified CNTs were mixed with the PS I-BM modified CNTs and incubated for two hours. The reaction was terminated by washing of the excess reagents as described above. The AFM images in Figure 4 illustrate the formation of cross linked junctions between CNTs mediated by the bipolar mutant PS I. The observed formation of a T-junction in hybrid CNT-PS I-CNT-junctions is a clear indication for a cross linking by the bipolar mutant PS I. It should be noted that no such T-structures were detected in the AFM images of the hybrid CNT systems when single sided PS I mutants were used (see Fig. 2). The higher density of the single mutant PS I at the end of the CNTs in Figure 2A, however, agrees well with the assumption that for both single and bipolar mutant PS I the covalent conjugation of the PS I to the CNTs is very efficient at the tips of the CNTs (see circle in Fig. 4B).

Figure 5 shows a fabricated device where bipolar mutants of PS I were contacted on one side by a metal electrode and on the other side by CNTs. To this end, gold islands with 20 micrometer in diameter were defined on silicon surfaces using photolithography. BM-PS I were adsorbed onto the gold surface using the procedure as published in ref. [5].

A monolayer of the PS I protein was self assembled on the gold electrodes by the incubation of PS I BM through the formation of a covalent sulfide bond between the Cys groups and the metal. As can be seen in Figure 5B, the PS I proteins uniformly cover the gold electrodes.[5] A drop of maleimide modified CNTs was then introduced to the modified surface and incubated for 4 hours with constant stirring. The unbound CNTs were washed away thoroughly and the surface was dried under gentle nitrogen flow. The modified CNTs bind through the maleimide moiety to the second Cys group at the open end of PS I. CNTs, which were longer than 2.5 μm, bridged the gap between the two gold islands covered with PS I monolayer (Fig. 5A). The resistance of ten devices with a gap size of about 2.5 μm was measured. A uniform metallic resistance of about (300 +/– 30) Ω for all devices at room temperature and ambient condition was measured (Fig. 5C). It should be noted that samples with single sided mutants of PS I and without PS I proteins show a much larger resistance variation in the range between 200 Ω and 20 kΩ (data not shown). The experimental finding indicates that a good electronic coupling between the CNTs and the gold surface is mediated by covalent binding of PS I. The photocurrent across such a contact configuration was studied at a photon wavelength of λ = 680 nm (Fig. 5D). A low pressure of ~ 10^{-5} mbar ensured to avoid photodesorption effects.[37] For laser intensities below ~ 60 W cm^{-2}, the photocurrent depended linearly on the laser power (dashed line in Fig. 5D). For high laser intensities a saturation curve was found. It should be noted that ~ 60 W cm^{-2} is a rather low value, since for single CNTs a linear dependence has been reported up to a laser intensity of

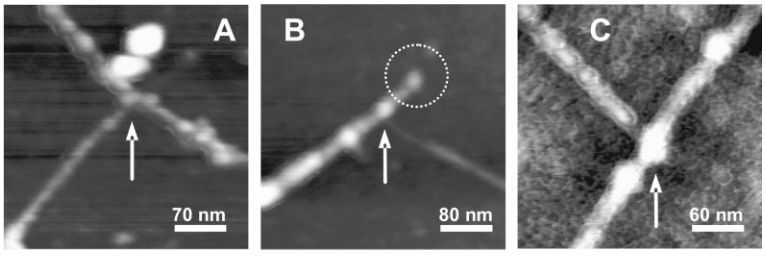

Figure 4. A)–C) AFM images taken of CNT-PS I-CNT hybrid junctions. The acid oxidation of CNTs generates defects at the side walls of the CNTs and at the tip of the CNTs. Latter results in binding of single PS I to the tip of the CNTs (circle in Fig. 4B) and in the formation of T-junctions of two CNTs via a BM PS I connection (arrows in all figures).

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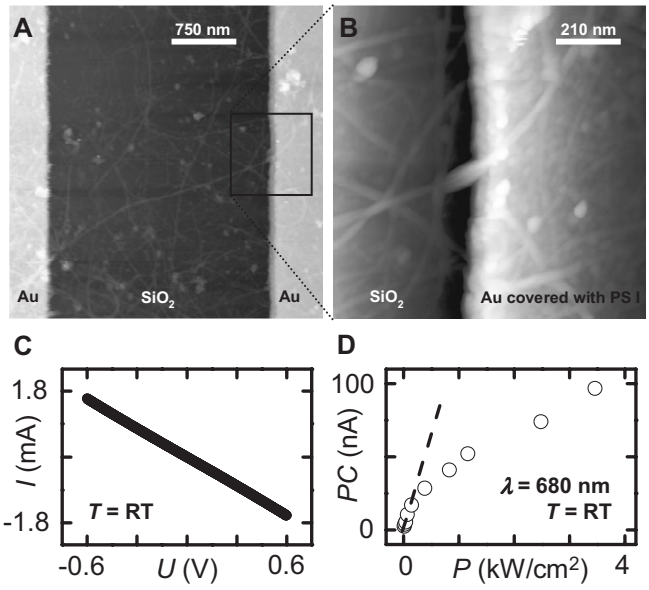

Figure 5. A) Maleimide modified CNTs bridging a 2.5 micrometer gold electrode gap. B) Close-up of the right gold electrode. A monolayer of BM PS I is formed on the gold surfaces, while only random PS I proteins can be detected on the SiO_2 surface. C) Typical *I–V* curve of such a device at room temperature (RT). D) Extra optically induced current (photocurrent) as a function of the laser intensity at $U = -0.6$ V. Dashed line is a guide to the eye.

~ 10 kW cm^{-2}.[17] The observation is surprising, since the typical density of the CNTs is rather low in samples as depicted in Figure 5A. Hereby, we attribute the saturation behaviour to the CNT-PS I-Au junction. However, future detailed studies are needed to elucidate the optoelectronic properties of such a circuit as a function of wavelength, temperature, and bias voltage.

In summary the present work demonstrates a chemical route for the fabrication of covalently coupled carbon nanotubes (CNTs) to the photosynthetic reaction center I (PS I). The various architectures of CNTs-PS I hybrids presented here can be used as building blocks for molecular optoelectronic circuits. Hybrid systems, consisting of CNTs and the PS I, promise new photo-induced transport phenomena, since the PS I is a robust cyanobacterial membrane protein with outstanding optical properties.

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