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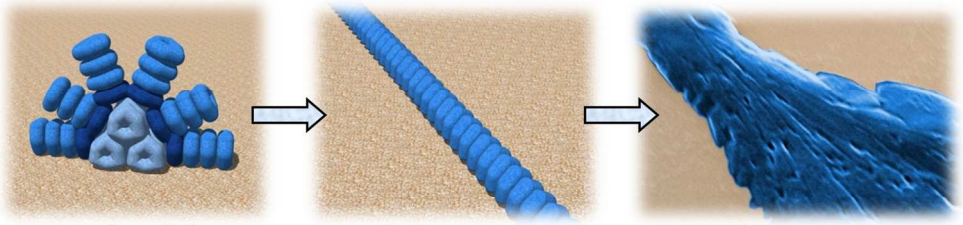

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Room-Temperature Biological Quantum Random Walk in Phycocyanin Nanowires

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Quantum nano-structures are likely to become primary elements of future devices. However, there are a number of significant scientific challenges to real world applications of quantum devices. These include de-coherence that erodes operation of a quantum device and control issues[1]. In nature, certain processes have been shown to use quantum mechanical processes for overcoming these barriers[2-4]. One well-known example is the high energy transmission efficiency of photosynthetic light harvesting complexes[5-7]. Utilizing such systems for fabricating nano-devices provides a new approach to creating self-assembled nano-energy guides. In this study, we use isolated Phycocyanin (PC) proteins that can self-assemble into bundles of nanowires. We show two methods for controlling the organization of the bundles. These nanowires exhibit long range quantum energy transfer through hundreds of proteins. Such results provide new efficient building blocks for coupling to nano-devices, and shed light on distribution and the efficiency of energy transfer mechanisms in biological systems and its quantum nature.

Broader context

Quantum nano-structures are likely to become primary elements of future devices. Going smaller below the 10 nm scale would help realizing nano-devices with high efficiency, low power consumption and high-speed. A novel approach to overcome fabrication limitations is by studying self-organized biological systems. Considering their functionality, light harvesting complexes known for high energy transmission efficiency and are an eminent candidate for this approach. In our work we used an isolated Phycobilisome component, the Phycocyanin trimer pigment-protein complex that participates in light harvesting and energy transfer in Cyanobacteria. We have isolated the proteins to realize large scale self-organized nanowires that form an exciton guide. These bundles can self-arrange as orthogonal dendrites by increasing the solution salt concentration or by patterning the structure of the dendrites. Exciton life-time shortening in the organized structures was measured, as well as a one micron broadening of the luminescence suggesting long range energy transfer. Such a long distance transfer and lifetime shortening may indicate strong coupling between groups of adjacent trimmers. These nanowires can open new horizons for the research in quantum biology and serve as fundamental building blocks for future quantum devices. For example, used as a transparent energy guide collecting energy from a window to a solar cell.

Introduction

The goal of miniaturizing electronic and optical devices to the 10 nm scale is facing great challenges[8]. At this size quantum phenomena start to play a major role even at ambient temperatures. Realizing such nano-devices may introduce high efficiency, low power consumption, high speed and smaller dimensions due to their molecular resolution. A novel approach to overcome the fabrication limitations is by studying self-organized biological systems. Considering its functionality, the photosynthetic system is an eminent candidate for this approach[9,10].

Recent experimental advances in various multi-chromophoric assemblies have raised the fascinating possibility that quantum coherent dynamics play a role in photosynthetic energy transfer,

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even at room temperature[9,11,12]. These remarkable findings indicate that a key to the survival of quantum coherence in this temperature regime is the emergence of correlated energetic fluctuations between different closely spaced chromophores, thus enabling the pigments to share the same coherent modes. Theoretical models show that these quantum phenomena improve the robustness and the efficiency of the system[13-16].

The exact mechanism of energy transfer through multi-chromophoric assembled light harvesting complexes is controversial. According to the classical approach, the exciton hops between two nearby sites due to dipole-dipole interactions. This approach described by the Förster Resonance Energy Transfer (FRET) mechanism[17]. Assuming that the strong coupling is directional the FRET model results in a one dimensional (1D) de-localization distance or 1D diffusion model for a high rate of multi-exciton generation. However, it is expected that when the system becomes ordered, using the Redfield equation[18] the dynamics of the off-diagonal density matrix element can be calculated giving a good estimation for the energy or electron transfer behavior. In these conditions due to symmetry directed assembly excited states become delocalized and enhanced quantum walk is predicted to take place[19-21]. This quantum mechanism treats is reliant upon the quantum coupling between two nearby sites[2]. Such de-localization of the wave-function requires a strong coupling that is known to exist at ambient temperatures in these systems. In this case the light-induced excitons are de-localized over an area larger than expected by the classical models[9,22,23].

In this work we used isolated Phycobilisome components, the Phycocyanin trimer protein complex (PC) that participates in light harvesting and energy transfer in Cyanobacteria. Phycobillisomes are organized in rods linked to the membranes through core proteins[24]. The rods are constructed from 3-6 PC hexameric units (formed by two trimers). The pigments embedded in the rods absorb the incident photons and create an exciton that is transferred to the core. We have isolated PC proteins to realize large scale self organized nanowires that form an exciton guide.

Results

PC trimers were isolated from the thermophilic cyanobacterium *Thermosynechococcus vulcanus*, in a procedure slightly modified from David et al.[25] (see Experimental). Isolated trimers were resuspended in a high phosphate buffer. Next, a drop of PC solution was dried over a solid substrate (glass, gold or silicon) at ambient conditions. When dried in appropriate conditions, PC trimers form bundles of nanowires. Figure 1a presents a high resolution TEM image of dried bundles on a TEM grid. Similar structures appear after washing a dried sample with water. Again, the trimers ordered as isolated bundles of nanowires surrounded by salt crystals (Figure 1b). The ordering that was achieved in the nano-scale creates nanowires as well as forming bundles at the micron-scale. The growth dynamic of the dendrites at the micro-scale is demonstrated in figures 1c-d in two stages of the growth.

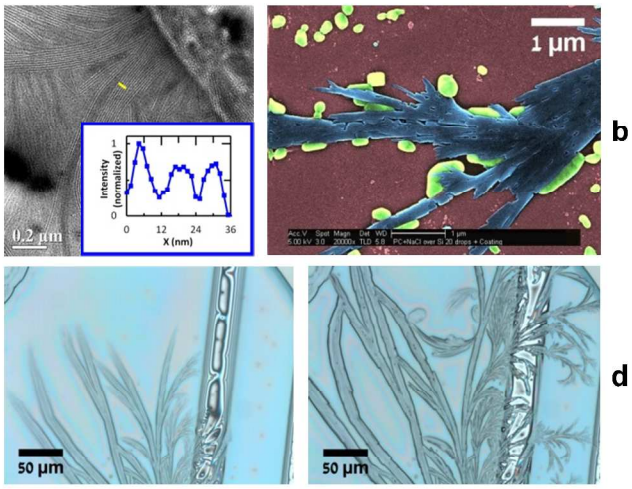

Fig. 1 Bundle formation (a) TEM micrograph of the self-assembled bundles of PC nanowires. Negative stain by ammonium molibdate highlights the white wires of the protein. The inset presents the periodic (12 nm) intensity profile cross-section through three PC-wires (along the yellow line). (b) Colored SEM image of dendrite of PC nanowires (blue) surrounded by salt crystals (green). The branches of the dendrite are flat and wide PC nanowires bundles. (c) Optical microscope image of PC dendrite over silicon substrate, still in a wet ambient of PC solution. The growth of the branches can be observed in an image that was taken few minutes later (d). See also the growth movie at supplementary material.

For applications use, a controlled organization of the bundles growth direction is needed. We have found two methods for organizing PC dendrites. The first method is by using a high concentration salt solution. In this case we obtained orthogonal branches of proteins covered by a salt-rich layer as shown at Figure 2a. This method is simple and easy to perform, however the structure of the dendrites cannot be organized in a directed fashion, and the salt crystals can scatter the exciting light. The second method is etching micro-trenches in a silicon substrate and filling them with proteins by spin-coating. The proteins dry along the trenches as shown in Figure 2b and 2c and controlled directionality is achieved.

Spectroscopic measurements were carried out on both solutions and dried samples excited by 532 nm wavelength light. The solutions had a typical photoluminescence peak wavelength of 650-670 nm depending on the concentration of the solution. At higher concentrations the peak shifted to the red, probably due to the combination of re-absorption processes and protein aggregation. Scanning of the dried sample with a confocal microscope and averaging the luminescence spectrum over a spot

showed that the sample has three typical emission peaks, at 621 nm, 637 nm and around 660 nm. The intensity ratio between the red shifted peak (660 nm), and the two blue peaks varies as a function of the local organization as shown in Figure 3a and Figure 3b. We ascribe the enhancement of the red 660 nm peak to more highly organized structures[26]. In such organized structures the lifetime of the excitation should be influenced by super radiance effects[27].

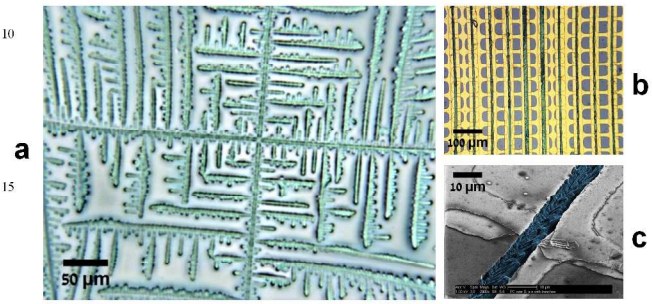

Fig. 2 Ordering the bundles (a) Optical microscope image of PC dendrite over glass substrate. The orthogonal dendrite was obtained by adding salts to the PC solution. (b) Optic microscope image of silicon substrate with micro-trenches filled with PC (blue) by spin-coating. (c) Colored SEM image of the same sample shows that the directionality of the bundle (blue) is determined by the orientation of the trench.

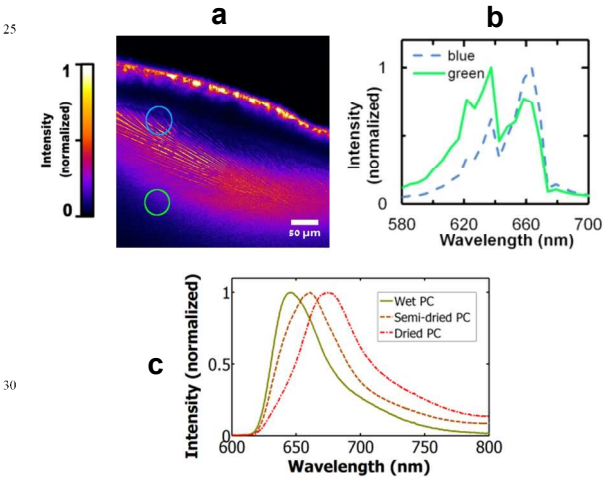

Fig. 3 Optical spectra (a) False color confocal microscope image of dried sample of PC over glass substrate shows straight branches of PC nanowires bundles. Sample is scanned by a 561 nm wavelength laser and luminescence is collected from 580 nm to 700 nm. (b) The averaged spectrum of two spots, blue and green, shows that more ordered structures exhibit relatively higher intensities at 660 nm which implies that this peak is attributed to ordered structures. (c) Luminescence spectrums of an entire PC sample that were taken during drying. The spectrum shows a clear red-shift of the peak. The peak starts at 645 nm, continue to 660 nm and ends at 675 nm.

Figure 4a presents time-resolved measurements of the photoluminescence of the solution, the dried samples and semi-dried sample indicating a lifetime of 1.15±0.1 ns, 0.4±0.1 ns and 0.6±0.1 ns, respectively. The dried samples are the most ordered ones and indeed the excited state lifetime (blue line) is short with respect to the solution lifetime by a factor of three (red line). In the semi-dried sample where the ordered structure is not fully developed (see Figure 1c), and therefore the order should be preserved only for short ranges, the lifetime is shortened only by a factor of two (purple line). Note that shortening of the life by the factor of 3 time fits the number you would expect, taking into account strong nearest neighbours coupling in two dimensional sheets (8 nearest neighbours) using the Redfield formulation[28] (figure 4b).

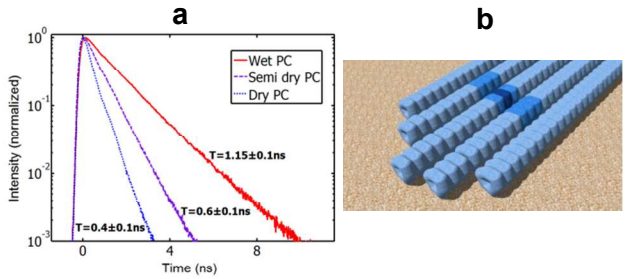

Fig. 4 Time-resolved measurements (a) Time-resolved measurements of the luminescence shows dependency of the exciton lifetime constant on degree of organization. The decay lifetime in the PC solution (red) is 1.15 ns comparing to the dried sample of PC (blue) that has a lifetime of 0.4 ns. Semi-dried solution (purple) shows a time constant of 0.6 ns that we ascribe to lower degree of organization as compared to the dried sample. The time constants were estimated using a fit to early time decay rates. The factor of 3 in shortening of the life time fits a strong nearest neighbours coupling in 2D bundles (8 nearest neighbors). Quenching of the surface was contradicted by changing the substrate, see results at supplementary material. (b) Schematic drawing of 5 PC nanowires arranged over surface. The 8 nearest neighbours mentioned before are highlighted in dark blue.

The change in the lifetime as a result of the ordering of the trimers in closed packed nanowires suggests that the delocalization length would be influenced as well. We studied the energy transfer mechanisms using a dual probe Near-field Scanning Optical Microscope (NSOM) system that allows for independent positioning and scanning of both tips[29]. The PC solution samples were dried over a glass substrate. We located a branch of PC wires (shown in Figure 5a), illuminated a fixed point with a 15 mW 532 nm laser through one cantilevered fiber probe and scanned with the second NSOM tip. The actual incident power is much lower, around 10nW due to many losses along the system and due to optic attenuator that was placed along the optic axis. Going to higher laser power did not affect the luminescence map. Both tips were in AFM feedback on the sample. Despite this, there is some leakage and scattering of the 532 nm excitation light adjacent to the primary excitation point. Therefore, both an excitation map and a luminescence map were taken from the same area using tip-scanning mode, where the sample is kept stationary relative to the excitation point. The excitation map with the scattering profile is shown in Figure 5b. Figure 5c presents the luminescence map created by a second scan where we filtered out the excitation flux using two laser blocking filters at 532 nm. Comparing excitation to luminescence was done by showing the each relative intensity along a transverse cross-section at y=9.7 µm (normalized results are shown in Figure 5d). In this area the luminescence graph is wider by 1-2 µm as compared to the excitation graph. There are fluctuations in the width of the luminescence spot that we ascribe to bundles defects (see supplementary material). For reference we have measured a sample with dense aggregates of CdSe luminescent nano-crystals (NCs) using the same system. The NCs

have similar luminescence behaviour as the PC protein with emission at 610nm. Nevertheless, no broadening of the signal was observed. The detector used for the measurements is an avalanche photodiode usually used for Raman measurements with linear response in all the measurement intensities. Moreover, a linear ratio between excitation intensity and luminescence intensity was measured at PC solution. Therefore, the above results suggest that for the ordered structure the energy can be transferred to a distance of 1-2 μm before emitting in the red spectra range.

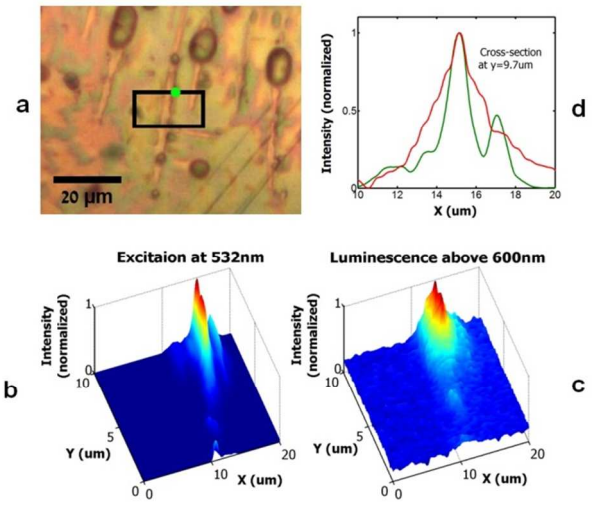

Fig. 5 Energy transfer (a) Optical microscope image of PC nanowires branches surrounded by some salt crystals (dark ovals shapes). This sample was scanned by two probe NSOM system for measuring energy transferring. Excitation was done by a 532 nm wavelength laser through a 150 nm diameter NSOM tip and detection was done with a multimode fiber with a 250 nm diameter tip. Excitation was done at the green circle and collecting was done within the black frame. When comparing the excitation distribution (b) and the luminescence distribution (c) clear broadening is obtained. (d) Cross-section of these two graphs at y=9.7 μm shows that the luminescence (red) Full-Width-Half-Maximum (FWHM) is wider than the excitation (green) FWHM in more than 2 μm. This result is attributed to energy transfer through the PC structure. For more detailed results see the supplementary material.

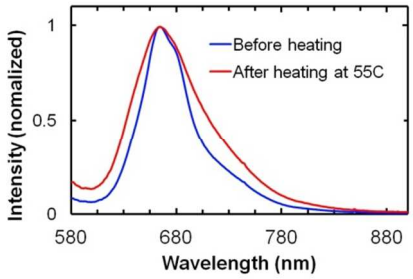

Fig. 6 Sample stability Luminescence graph of dried PC sample, before and after heating to 55 °C for an hour. The similarity of the two graphs indicates the stability of the PC. For additional stability measurements see the supplementary material.

For applications use the nanowires should be stable. The protein used here are very stable. The spectrum of the dried samples was measured before and after one hour heating to 55 °C. Figure 6 shows that the luminescence peak was not changed significantly by the heating procedure.

Discussion

We have shown that the PC trimers form long nanowires that can be hundreds of microns long. The nanowires tend to aggregate into bundles. Taking into account that the PC trimer diameter is around 10 nm and their thickness is around 3 nm[24], each wire should contain thousands of trimers. Each bundle includes tens to hundreds of nanowires. The distance between the nanowires in Figure 1a is 11-12 nm and therefore the gap between them should be between 1-2 nm.

The growth of the nanowires is believed to occur due to the modification of the protein environment. *In-vivo*, trimers are part of the phycobilisome assembly that contains other protein components (linker protein) that can control its growth[25,30]. In our preparations, all linker proteins have been removed and only PC is present. The salt, in this case, provides the appropriate environment for the wire growth. This could also explain the ordered straight nanowires obtained at high salt concentration.

The exciton lifetime was measured to be larger than a nano-second in solution and around 0.5 nano-seconds for the ordered structure. Taking into account that the energy transition time between two adjacent PC trimers is in the pico-seconds range[31], one can assume that there are around 100 exciton transfer steps before a photon is emitted. The NSOM measurement of energy transfer showed mainly a transverse energy transfer. In our case we would expect an energy transition at nanowires bundles both longitudinally and transversally. Assuming that the exciton propagation in one direction is decoupled from the other direction allows us to treat this problem as a 1D random-walk. According to the classical FRET mechanism, in the case of 100 steps, the expected width of emission will be wider by around 50nm (standard deviation 5). This approximation could not explain the long distance energy transfer. Our results suggest that additional mechanisms take place. Such a transmission could be ascribed to quantum super-transition where an increase of an order of magnitude in distance could take place[32] or to biological quantum random walk where the number of expected steps tends to scale linearly with the number of steps (around 0.7μm taking 100 steps of 10nm)[33,34]. In this case the strong coupling in the transverse direction is expected, as parallel dipole interaction is higher than head-tail configuration[35]. The large anisotropy we measured therefore could be ascribed to the strong transverse coupling or to anisotropy of the NSOM tip. The NSOM tip anisotropy is usually smaller than 10%. When efficient, both super-transition and quantum random walk would increase the transmission distance to the micron scale and we cannot distinguish between the two mechanisms within our resolution.

The results presented here also provide interesting insight into the function of phycobilins in light harvesting processes *in vivo*. Despite intense efforts the structure of the light harvesting phycobillin assembly, the three dimensional structure of the phycobilisome, is still unclear[36]. Analysis of the isolated phycobilisome structure requires the presence of high concentrations of phosphate ions, since in their absence the complex quickly disassembles. There is microscopic evidence that suggests that the phycobilisome attached to the thylakoid membrane is not of a fixed structure but rather a looser assembly

of phycobiliproteins appressed between two thylakoid membrane surfaces. This type of organization will create structures in which the spacing and orientation of pigments is randomized to a large extent. In effect, such an organization will generate a rough energy landscape that will support the quantum random-walk processes demonstrated here. The energy collected by light harvesting systems is transferred to photochemical reaction centers embedded in the thylakoid membranes. These photosystems are distributed in distances of a few nanometers from each other (Ziv Reich, personal communication). The thylakoid membranes extend throughout the cyanobacterial cell, creating sheaths that can be a micron long. In such geometry, a single excitation traveling through quantum random-walk processes can be utilized by any one of the thousands of reaction centers within the membrane. The results presented here show that phycocyanin rods have the ability to transfer absorbed energy vertically down the rod substructure, as well as horizontally, between rods. If the phycobilisomes are tightly packed on the membrane, rods of one phycobilisome may be close enough to rods of the adjacent phycobilisome and energy transfer can then proceed to diffuse over great distances until exciting a single reaction center.

The shorter lifetime of the ordered sample comparing to the solution may indicate that the lifetime measurements are related to collective super-radiant emission[32]. This quantum effect implies that the long range of energy transfer is indeed related to the quantum super-transition theory (described in the background section). We believe that the more the structure is organized the higher the coupling between the PCs and therefore the life-time should decrease continuously during drying process. The suggested mechanism requires a non-local exciton, a result which agrees with recent findings in a purple-bacteria light harvesting complexes[37] and LH2 complexes[38].

Experimental

T. vulcanus cells were grown in a 10 liter temperature-controlled growth chamber on BG11 medium supplemented with 5% CO_2 in air at 55 °C, with fluorescent lamp illumination. Cells were grown for 5 to 7 days before collection by centrifugation. Trimeric PC was obtained by resuspending the cells in isolation buffer (20 mM Tris, 10 mM $MgCl_2$ and 10 mM $CaCl_2$, pH 8) and treating with lysozyme (1 mg/ml) for 1 hr at 50 °C, before passing through a French Pressure cell at 1500 p.s.i.. Following a 25 min centrifugation at 15,000 rpm, the blue supernatant was filtrated in 50KDa (Amicon) three times, each time the supernatant was diluted with Buffer A (20 mM Tris, pH 8). The supernatant was filtrated in 0.22 µm MILLEX-HV syringe driven filter. The filtered supernatant was further separated by two rounds of high pressure anion exchange chromatography. Fractions were characterized by absorption spectroscopy in order to select for samples containing pure PC. The resulting pure PC was dialysed against 20mM Tris pH 8 and then concentrated by ultrafiltration (Millipore).

The glass substrates are standard microscope slides while for gold substrates we evaporated 10 nm thin layer of chrome and 100 nm of gold subsequently over the same kind of slide. The silicon substrates that were used are (100) n-type silicon. 5-10 µm width trenches were fabricated by optic lithography process using SU-8 photoresist. After the development of the photoresist we etched the sample by an RIE process to a depth of 3.35 µm and removed the photoresist by hot acetone. Finally, before assembling we cleaned the samples with acetone and ethanol.

The dried samples were prepared by dropping a 3-30 µl PC solution over the sample and drying it at room temperature. The trenches samples were spun at 4000 RPM right after laying the drop to flat the drop.

SEM images were taken with a FEI Sirion system at 1-20 kV using both high resolution mode and ultra high resolution mode. Some of the samples, like Figure 1b, were sputtered with gold. A 400-mesh carbon-coated grid was placed on a 20 µl PC drop for 2 min at room temperature and blotted with a filter paper to remove excess solution. The sample was chemically stained by placing the grid on a 20 µl drop of 3% amonium molybdate for 2 s and blotting, then placing the grid on another 20 µl drop of 3% amonium molybdate for 2 min, followed by blotting and air-drying. Specimens were examined in a Philips CM120 TEM operating at 120 kV. Images were recorded digitally on a Gatan MultiScan 791 camera using the DigitalMicrograph software (Gatan, U.K.).

The spectral measurements were done using an Ocean Optics USB4000 spectrometer where the samples are illuminated with a 532 nm wavelength laser at a power of 10-20 mW. We used a Leica SP5 confocal microscope to scan with a 561 nm wavelength laser. The NSOM measurements were done using a Nanonics MultiView 4000 while exciting with a 532 nm laser through an optical fiber of 150 nm diameter and with a 250 nm diameter multimode fiber NSOM tip for detection. The output power was less than 10 nW due to attenuating (the laser power was 15 mW). The time-resolved fluorescent measurements were carried out using a time-correlated single-photon counting (TCSPC) approach using Edinburgh Instruments FLS920 Fluorescence Spectrometer with a TCC900 TCSPC card. Samples were excited using a Fianium SC400 super continuum laser monochromatized at 532 nm. The emission from the sample was collected at a right angle, through a long-pass filter and a monochromator to suppress the scattering from excitation source, and collected using a Hamamatsu H10720 high speed PMT.

Figures 1b and 2c were painted by standard image processing tools. Optical microscope images were aesthetically improved by changing brightness and contrast. The data of Figure 5c was filtered by low pass filters.

Conclusions

In this study we showed that drying isolated PC trimers results in the formation of bundles of PC nanowires. These bundles can self arrange as orthogonal dendrites by increasing the salt concentration of the solution. Patterning the structure of the dendrites is also possible by filling micro-trenches with spin-coating. Exciton lifetime shortening at organized structures was measured and broadening of luminescence mapping in comparison to excitation suggests energy transfer at distances up to one micron. Such a long distance transfer and lifetime shortening may indicate strong coupling between the trimers due to quantum mechanics, which plays a role in creating the high efficiency of photosynthesis. These biological nanowires can serve as fundamental building blocks for future quantum devices

and open new horizons for the research in quantum biology.

Acknowledgment

The confocal microscopy imaging was done at The Confocal Unit in the Institute for Life Sciences, HUJI, by Dr. Naomi Melamed-Book. Substrates fabrication and SEM characterization were done at the Centre for Nano-science and Nano-technology, HUJI, with the assistance of the local staff. Two probe NSOM measurements were done at Nanonics Imaging Ltd. thanks to the assistance of Prof. Aaron Lewis. Time resolved measurements were carried out at the lab of Prof. Uri Banin from The Institute of Chemistry and the Center for Nano-science and Nano-technology, HUJI. Dr. Ellina Kesselman and Dganit Danino are thanked for their assistance in obtaining the negative stained TEM images. This work was supported by the US-Israel Bi-National Science Foundation (2009406 to N.A.) and the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities (1576/12 to N.A.).

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