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Utilizing redox-chemistry to elucidate the nature of exciton transitions in supramolecular dye nanotubes

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Supramolecular assemblies that interact with light have recently garnered much interest as well-defined nanoscale materials for electronic excitation energy collection and transport. However, to control such complex systems it is essential to understand how their various parts interact and whether these interactions result in coherently shared excited states (excitons) or in diffusive energy transport between them. Here, we address this by studying a model system consisting of two concentric cylindrical dye aggregates in a light-harvesting nanotube. Through selective chemistry we are able to unambiguously determine the supramolecular origin of the observed excitonic transitions. These results required the development of a new theoretical model of the supramolecular structure of the assembly. Our results demonstrate that the two cylinders of the nanotube have distinct spectral responses and are best described as two separate, weakly coupled excitonic systems. Understanding such interactions is critical to the control of energy transfer on a molecular scale, a goal in various applications ranging from artificial photosynthesis to molecular electronics.

Nanostructures of self-assembled organic molecules may find use as well-defined building blocks for light-harvesting and other optoelectronic applications^{1–17}. A particularly intriguing class of artificial supramolecular systems comprises double-walled nanotubular dye aggregates (light-harvesting nanotubes) composed of close-packed amphiphilic cyanine dyes¹⁸. Like the highly efficient photosynthetic antenna systems (chlorosomes) of green sulfur bacteria^{19–21}, these artificial dye nanotubes contain thousands of molecules packed in a cylindrical geometry and have diameters on the order of 10 nm and lengths that may extend to several micrometres^{22,23}.

In particular, it was recently shown that nanotubular aggregates composed of the cyanine dye 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-diocetylbenzimidacarbocyanine¹⁸ (abbreviated C8S3, Fig. 1a) prepared in a water/methanol solution^{24,25} (illustrated schematically in Fig. 1b) have a remarkably uniform supramolecular structure²³. They provide an excellent model system for studying excitonic interactions between two multichromophoric systems, as they are composed of two well-defined concentric nanotubes separated by ~4 nm (refs 22,23,26).

The small diameter and large length of the nanotubes render them ideal as potential building components for use in nanotechnology. Moreover, they are of interest from the perspective of fundamental nanoscience as their unique properties arise not from their individual molecular components, but rather from the collective properties of the supramolecular assembly. As with natural light-harvesting antenna systems, the strong interactions between the molecules resulting from their close-packing lead to new electronic excitations. These new excited states, Frenkel excitons, are delocalized over a range of molecules rather than localized

on any individual molecule^{27–29}. The nature of these states depends intimately on the details of the molecular packing and thus on the supramolecular structure^{1,12,30–32}. Here, the specific packing yields several strongly absorbing exciton transitions that are narrowed and redshifted with respect to the monomer transition (Fig. 1c), a spectral signature characteristic of (nanotubular) J-aggregates.

On elucidating how the structural details determine the optical properties, one can envision tuning the properties of materials by altering the molecular packing within the nanoscale structure of the assembly. In the past, these double-walled nanoscale systems have generally been treated—by experiment^{24,26,33,34} and theory^{35,36}—as two distinct excitonic systems that are only weakly coupled; one is composed of the close-packed dye molecules in the inner-wall cylinder and the other is composed of the close-packed dye molecules in the outer-wall cylinder of the nanotube (Fig. 1b). Consequently, the two prominent transition bands in the absorption spectrum of the assembly, labelled bands (1) and (2) in Fig. 1c, have been previously assumed to belong to the inner-wall and outer-wall cylinders, respectively^{24–26,35,37}. The rather broad transition band (3) is assumed to contain two overlapping bands from each of the cylinders³⁵. The origins of transition bands (4) and (5) are unknown as yet, and bands (6) and (7) have been assumed to be associated with dye monomer residues as they coincide with the dye monomer absorption bands (black line).

Recent two-dimensional electronic spectroscopy studies have suggested that such double-walled aggregates cannot be treated as two separate subsystems, however, and instead should be regarded as one strongly electronically coupled system^{38–42}. This controversy shows that the treatment of supramolecular assemblies in close proximity to one another (that is, with a molecular-scale

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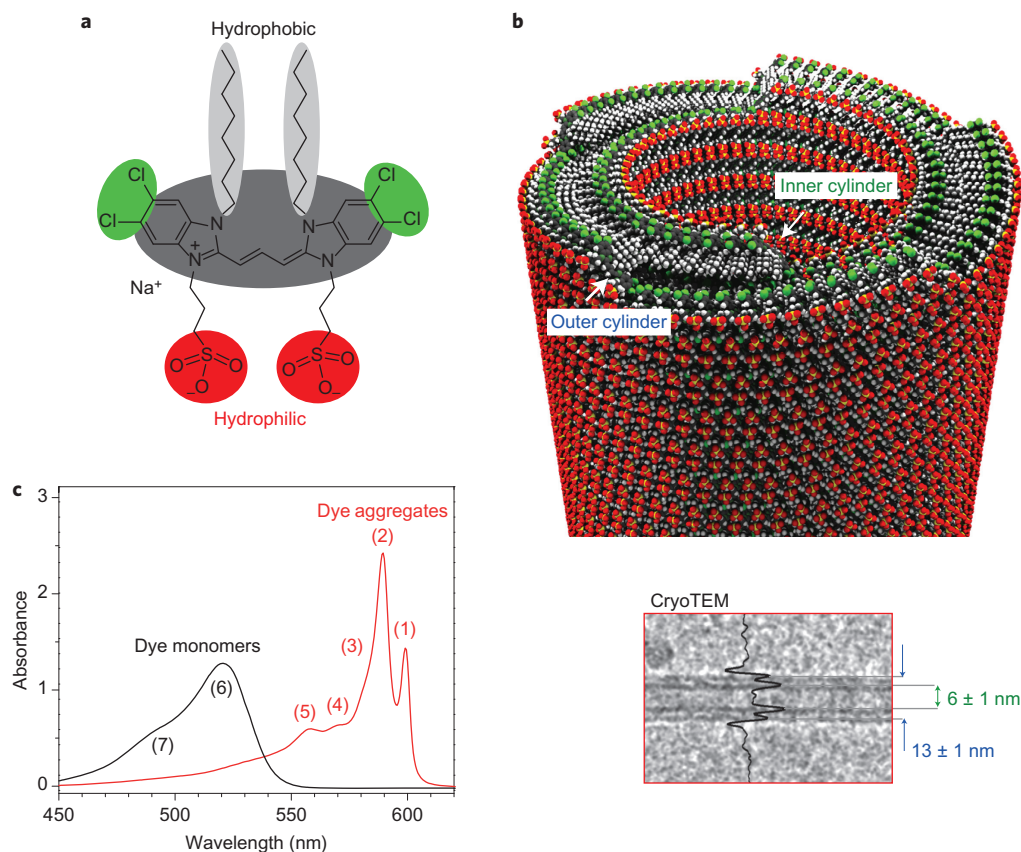


Figure 1 | Light-harvesting nanotube consisting of double-walled cylindrical aggregates of amphiphilic cyanine dye molecules. **a**, Amphiphilic dye monomer C8S3. **b**, Schematic of the self-assembled light-harvesting nanotube (for clarity using only one molecule per unit cell): double-walled structure with the hydrophilic sulfonate groups (red) on the exterior, the hydrophobic alkyl chains (light grey) in the interior of the bilayer and the cyanine dye chromophore (dark grey). The cryoTEM micrograph (see also ref. 26) depicts the double-walled character of the light-harvesting nanotube. **c**, Absorption spectra of dye monomers (black) dissolved in methanol (no aggregation) and nanotubular dye aggregates prepared in water/methanol (red).

separation) remains an open question. Should such systems be viewed as two weakly coupled quantum subsystems, each with its own electronic eigenstates, or as a single supramolecular quantum system? Addressing this question is critical for gaining better insight into how photoexcitations can be directed and amplified using assemblies of molecules in light-harvesting applications. Straightforward and easily accessible experimental techniques are desirable for addressing this fundamental question directly.

In this Article, we show that simple oxidation chemistry can be used as an elegant tool to address this pivotal question by effectively uncoupling the exciton transitions within a complex multicomponent supramolecular system. This is accomplished by monitoring the changes in the excitonic transitions upon chemical oxidation of the dye molecules preferentially located in one cylinder of the double-walled nanotube, essentially turning off the optical response of the dye in that cylinder. This allows for a direct comparison of the spectra originating from an isolated, uncoupled cylinder with those of the full double-walled nanotube. Moreover, this isolated spectrum presents a well-defined reference point for new model calculations that give new and detailed insights into the supramolecular structure of the aggregate. The oxidation results are confirmed using a complementary experimental approach that perturbs the self-assembled structure using a new so-called flash-dilution technique (see Methods). Our experimental results are compared with numerical simulations of absorption spectra for both the isolated uncoupled cylinder and the full double-walled nanotube system. These simulations, based on a

Frenkel exciton model, predict electronic absorption spectra for the single- and double-walled nanotube systems that are in agreement with our experimental findings.

Results and discussion

Previous spectro-electrochemical studies have shown that the oxidation of these nanotubular aggregates lead directly to a strong loss of transition band (2) and correspondingly smaller decrease of transition band (1) (labelling of bands according to Fig. 1c)^{24,25,37}. Assuming that these two bands arise from the two cylinders in the double-walled nanotube, this would be consistent with one cylinder being more readily oxidized than the other. Here, this approach is taken to its natural limit in an effort to completely oxidize one cylinder while maintaining the characteristic double-walled morphology of the nanotube.

Chemical oxidation in solution. The nanotubes were chemically oxidized in solution using Ag^+ as an external oxidizing agent. It has been demonstrated that adding AgNO_3 to an aggregate solution leads to the reduction of the silver ions (Ag^+) to silver metal (Ag^0), with a concurrent oxidation of the dye molecules of the nanotube²⁶. The loss of electrons from the π -conjugated system of the dye chromophores upon oxidation leads to the observed change in the absorption spectrum and a decrease in the exciton bands^{24–26,37}. Thus, chemical oxidation can be used as an elegant and convenient tool to eliminate the absorption of the dye molecules localized within the region of the double-walled nanotubular aggregate that is most readily oxidized.

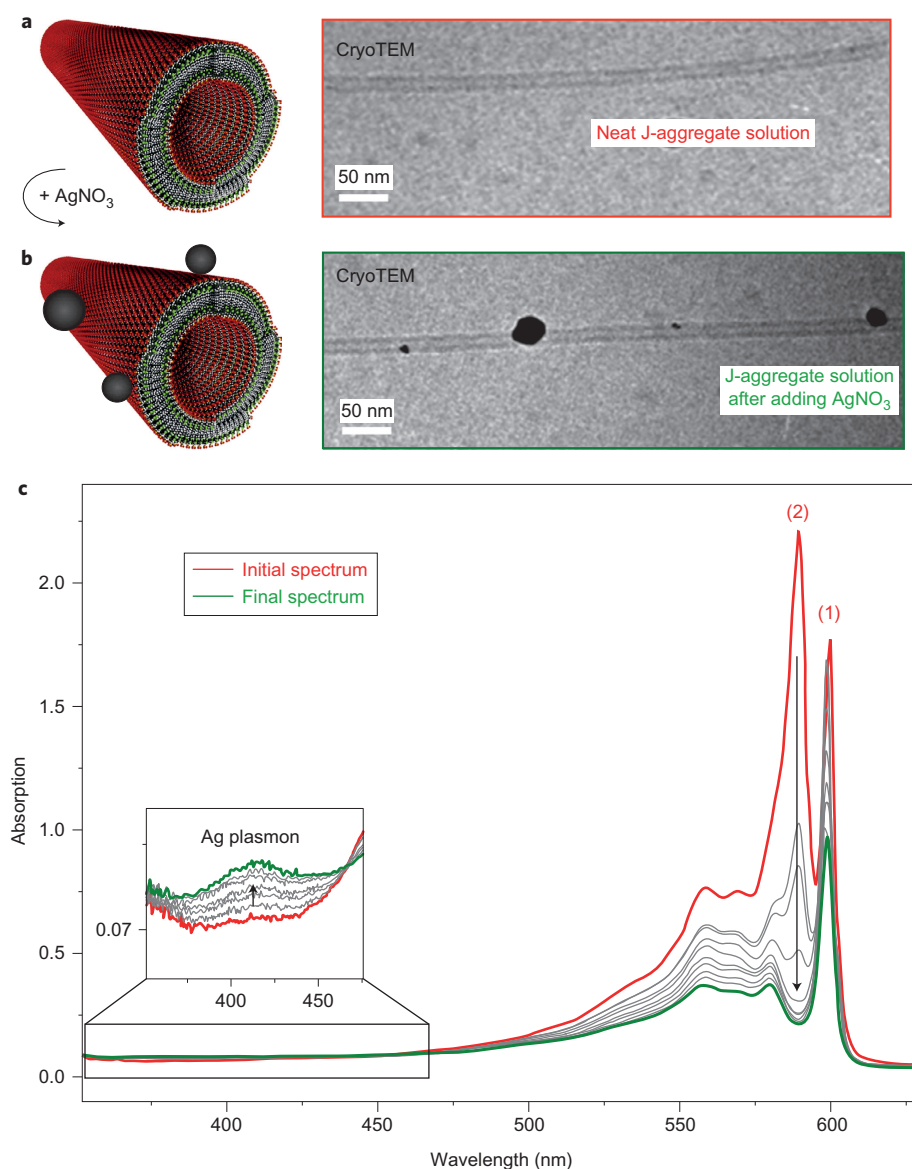


Figure 2 | Chemical oxidation of light-harvesting nanotubes in solution. **a,b**, Representative cryoTEM micrographs (see also ref. 26) of the neat nanotubular dye aggregate solution without AgNO_3 (**a**, red box) and with AgNO_3 (**b**, green box); see also ref. 26. **c**, Absorption spectra of the nanotubes in solution. Spectrum for the neat nanotube solution is shown in red. Upon adding AgNO_3 , the spectra (grey) decrease continuously over 6 h (spectra taken every ~ 30 min) towards the final trace (green). Inset: increased silver plasmon absorption correlates with a decrease in nanotube absorption.

It is critical that the oxidation chemistry does not perturb the double-walled morphology of the nanotubes. The morphology of the tubes before and after oxidation can be verified by cryogenic electron transmission microscopy (cryoTEM) (Fig. 2a,b). The nanotubular nature of the aggregate is clearly visible in both electron micrograph images and appears unchanged following oxidation (Supplementary Section S1). The only change after adding AgNO_3 is the appearance of silver nanostructures in direct contact with the nanotube, consistent with oxidation of the dye in the outer cylinder²⁶.

Optical properties following chemical oxidation. Although the oxidation does not significantly affect the morphology of the double-walled nanotubes, it has a strong effect on their optical properties. Figure 2c shows the changes in the absorption spectrum of a solution of nanotubular dye aggregates after adding AgNO_3 . The spectra clearly demonstrate that, as the redox reaction proceeds, there is a loss in the total absorption of the aggregate. This loss is directly correlated with increased absorption in the region of the

silver plasmon absorption at ~ 420 nm (Fig. 2c, inset). Transition band (2), at ~ 589 nm, exhibits a stronger decrease than transition band (1), at ~ 599 nm. From the final spectra in the data set depicted in Fig. 2c, it appears that the contribution of transition band (2) has been eliminated from the spectrum. To assess the number of chemical species contributing to the absorption spectrum of the double-walled nanotubes, the spectral changes within this data set (Fig. 2c) were analysed by singular value decomposition (SVD)⁴³. SVD analysis results in only two basis spectra with singular values that are significantly different from zero (Supplementary Section S2), so a simple linear combination of only two basis functions therefore reproduces all the spectra in this data set. This is a clear indication that the spectrum of the full double-walled nanotube system consists of only two separate contributing species.

These results show unambiguously that the double-walled nanotube system can be treated as two electronically separate cylindrical aggregate systems, one in the inner wall and the other in the outer wall. The two cylinders can be considered as weakly coupled,

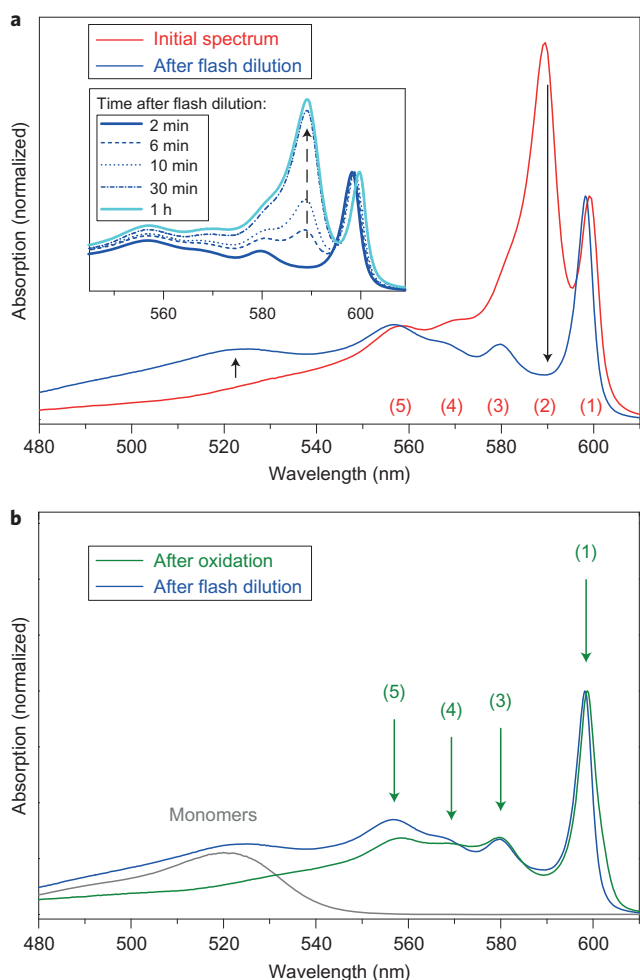


Figure 3 | Isolated absorption spectrum of the inner-wall cylinder of the light-harvesting nanotubes. **a**, Red, neat nanotubular dye aggregate solution. Blue, nanotubular dye aggregate solution following flash dilution (spectrum taken immediately after flash dilution); nanotube absorption has decreased, together with a corresponding increase in monomer absorbance (black arrows). Inset: diluted nanotubular dye aggregate solution (dark blue, spectrum taken immediately after flash dilution), within ~ 1 h after flash dilution (blue dashed lines), and normalized absorption spectrum of diluted solution after ~ 1 h (light blue). Unlike in the oxidation experiments, changes with dilution are transient: the main transition band (2) rapidly grows back into the spectrum and is finally stable after 1 h. **b**, Comparison of absorption spectra upon oxidation and flash-dilution experiments: nanotubular dye aggregate solution upon flash dilution (blue); nanotubular dye aggregate solution upon chemical oxidation using AgNO_3 (green); dye monomer solution (grey).

effectively uncoupled, because the position and shape of the transition bands in the absorption spectra do not change significantly before and after chemical oxidation. In contrast, significant changes in the spectrum would be expected for two strongly coupled systems. Our results demonstrate that the two aggregate systems of the double-walled dye nanotube are only weakly coupled. Therefore, the spectrum of this dye aggregate system can be simplified as the sum of the individual spectra of two cylindrical aggregates.

Optical properties upon flash dilution. Analysis of the spectral changes in Fig. 2c reveals that near the end of the reaction the contribution from one species has been completely eliminated, as further oxidation leads to a decrease in absorption amplitude but

not a change in the general spectral shape. (The last three spectra are identical except for the amplitude; Supplementary Section S3.) Consequently, this final spectrum (green line) can be assigned to the residual absorption of a single aggregate cylinder (in the presence of the other completely oxidized aggregate cylinder). To verify this, a second experiment consisting of flash dilution of the dye aggregates solution was used to isolate the spectrum of a single cylinder by a different means.

Dilution strongly perturbs the nanotubular dye aggregate; indeed, because of their self-assembled character they are highly sensitive to any environmental changes. This experiment has the advantage of being able to confirm the supramolecular origins of the transitions in the double-walled nanotube system, because one would expect the flash dilution to affect the dye located in the outer-wall cylinder of the nanotube to a greater degree than that of the inner-wall cylinder, as the outer-wall nanotube is exposed to the bulk solvent.

Neat dye aggregate solution was added abruptly to a water/methanol solution. Figure 3a shows the normalized absorption spectrum of the aggregate solution taken immediately after flash dilution (blue line) as well as the normalized absorption spectrum of the neat aggregate solution (red line). Upon flash dilution, the most dramatic change takes place for transition band (2), at 589 nm, which appears to have vanished completely. As the dilution should preferentially affect the outer-wall cylinder, the experiments give final evidence that exciton transition band (2) at 589 nm and exciton transition band (1) at 599 nm are assigned to the outer-wall and inner-wall cylinders, respectively. On the other hand, the increase upon flash dilution of the monomer absorption band at ~ 520 nm can be explained by dye molecules (preferentially located in the outer-wall cylinder) being dissolved into the bulk solution. In contrast to the increasing monomer absorption band at ~ 520 nm, the higher energy transition bands (3), (4) and (5) do not increase. This gives conclusive proof that transition bands (3), (4) and (5) cannot be assigned to other species such as dye monomers, but rather arise from the cylindrical nanotube system itself. It is possible that the flash dilution results in an isolated tube with different characteristics; however, the changes upon flash dilution are transient, with the same spectrum of the full double-walled nanotube system returning approximately an hour after dilution (Fig. 3a, inset).

The residual spectrum taken directly after flash dilution with methanol/water strongly resembles the final spectrum isolated by chemical oxidation, the only difference being the additional contribution from the monomer spectrum in the dilution experiment. The spectra of the inner-wall cylinder isolated from the two distinct experiments can be compared directly. Figure 3b shows the absorption spectrum from the diluted aggregate solution (blue line) as well as the isolated inner-wall spectrum from the oxidation experiments (green line). The spectra from the two experiments are nearly identical, with only a slight discrepancy around transition bands (4) and (5) at a wavelength of ~ 555 nm. The fact that the two spectra are nearly identical provides evidence that the spectrum of the inner-wall cylinder can be successfully isolated from the full double-walled nanotube system. These results demonstrate that easily accessible chemistry methods can be used to reduce the complexity of excitonic supramolecular systems.

In addition, the isolated spectrum of the inner wall (Fig. 3b) provides insights into details of the underlying supramolecular structure of complex cylindrical aggregates. Not only does this spectrum contain transition bands (1) and (3), but it is also evident that transition bands (4) and (5), which were previously of unknown origin, are also associated with the inner-wall cylinder. Determining the origin of these transitions, however, requires an extension of the geometries that have been used previously to successfully simulate the optical spectra of similar cylindrical aggregates^{31,35,44}. Within these

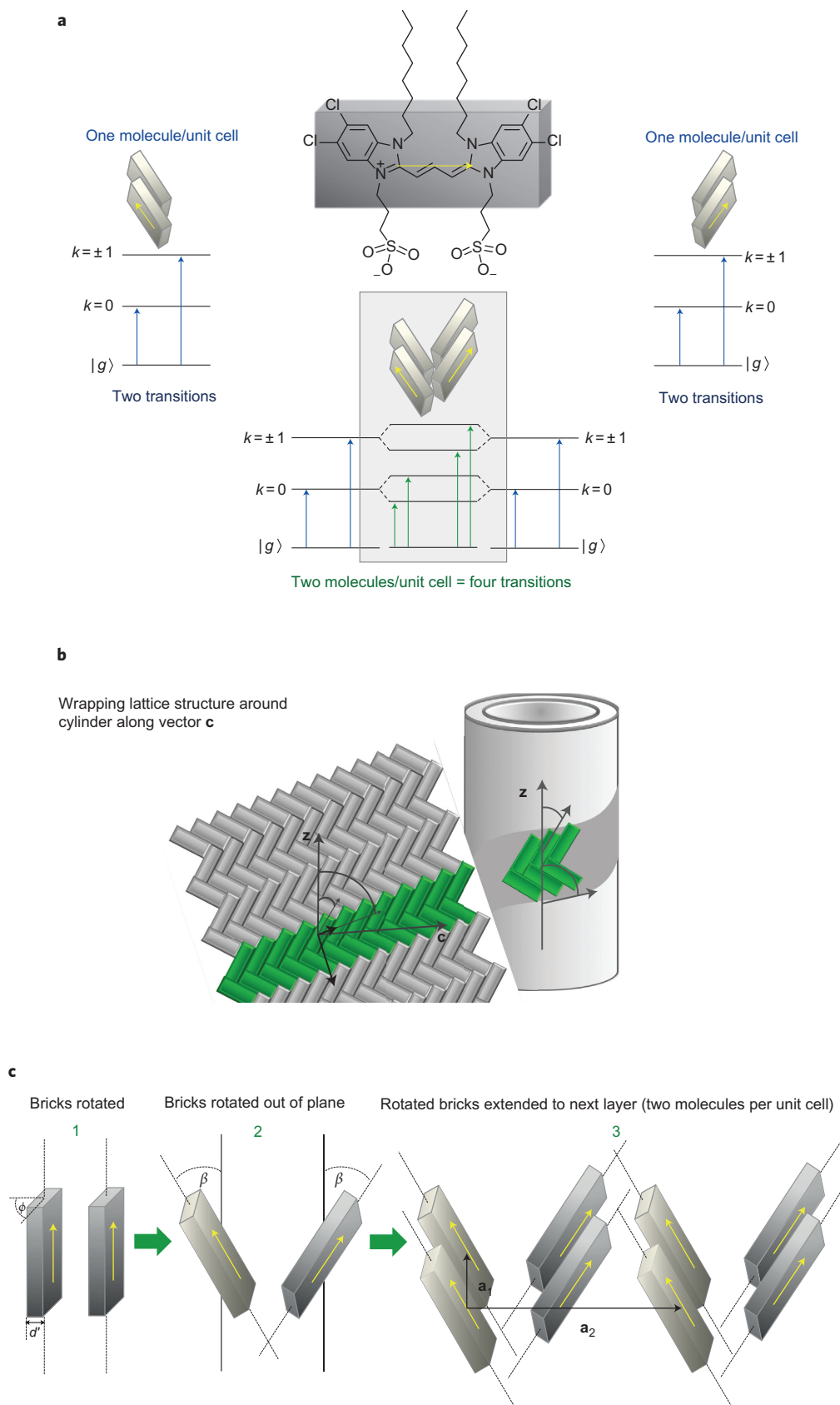


Figure 4 | Structural model for a light-harvesting nanotube and theoretical simulations of linear absorption spectra of nanotubes. a, Cartoon demonstrating the basic concept to explain four transitions in the isolated absorption spectrum of the inner-wall cylinder, going from a one molecule per unit cell structure (giving rise to two optical transitions from ground state $|g\rangle$ to excitonic states $|k\rangle$) to a two molecules per unit cell structure (four optical transitions). **b**, Schematic of herringbone structure with two molecules per unit cell, which is wrapped around a cylinder. **c**, Schematic of the two molecules per unit cell EHB structure for a cylindrical aggregate (rows have been pushed apart for clarity).

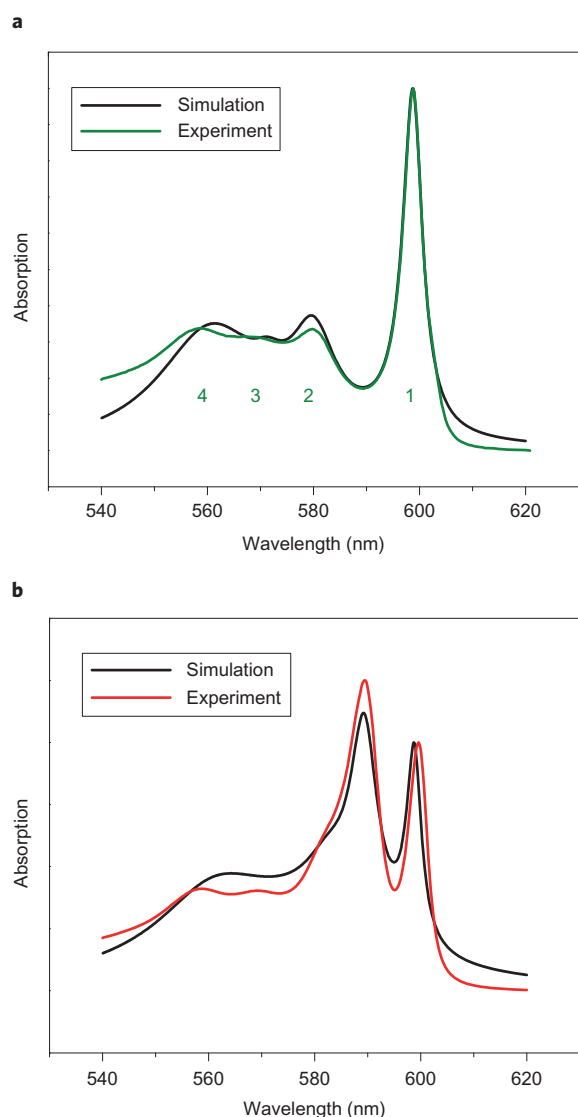


Figure 5 | Comparison of theoretical simulations with experimental absorption spectra. **a**, Isolated absorption spectrum of inner-wall cylinder (normalized), experiment (green) versus theory (black): simulated absorption spectrum of the inner-wall cylinder using the two molecules per unit cell EHB structure, yielding four optical transitions. Transitions have been broadened by Lorentzian lineshapes of appropriate width to facilitate comparison with experiment. **b**, Full spectrum of double-walled cylinder (normalized), experiment (red) versus theory (black): simulated spectrum using the two molecules per unit cell EHB structures (see Fig. 4) with appropriate geometrical parameters for both inner-wall cylinder and outer-wall cylinder, allowing for a total of eight (possibly degenerate) optical transitions. Cylinders are simulated as separate, uncoupled systems.

models, a simple one molecule per unit cell structure is assumed, with the molecules arranged in a planar bricklayer configuration that is then rolled onto a cylinder. As a consequence of the cylindrical symmetry, this model results in isotropic absorption spectra containing only two distinct peaks^{31,32,35}. The greater number of transition bands found above indicates that the building blocks of the structure for this inner-wall cylinder should contain more than just one monomer.

Structural model and simulations. To explain the number of experimentally observed transitions in the absorption spectrum of the inner-wall cylinder, its spectrum was simulated using a geometry

with two molecules per unit cell, yielding four optically allowed transitions (Fig. 4a). In contrast to the well-known bricklayer structure^{31,32,35}, a new structural model was designed using a herringbone structure, which is then wrapped around the cylindrical surface (Fig. 4b). For this new structure the molecules are no longer in plane, but are rotated (in alternating directions) out of plane in a geometry referred to as the extended herringbone-like (EHB) geometry (Fig. 4c). This novel arrangement was introduced to correctly reproduce the intensities of the high-energy transitions (4) and (5) found in the experiment, as this could not be accomplished with geometries where the molecules remain in plane (Supplementary Section S4). This structural model retains a high degree of π -stacking, as is common to many dye aggregates.

In addition to the spectrum of the inner-wall cylinder, the absorption spectrum of the double-walled nanotubular system was also simulated by treating the two cylinders as two separate, uncoupled systems. Here, both the inner-wall and outer-wall cylinders were modelled using the new EHB structure, rolled onto a cylindrical surface with the appropriate radius. A fitting procedure for the geometrical parameters (Supplementary Section S5) for both cylinders was used to optimize the agreement of the simulated spectrum with the experimentally obtained spectrum. The resulting two sets of optimal geometric parameters, together with the obtained narrow range of validity of these parameters, show that the supramolecular arrangements within both cylinders are not only nearly identical, but their geometries are also obtained to a high degree of accuracy (Supplementary Section S5). As shown in Fig. 5a,b, the simulations of the absorption spectra for the isolated inner-wall cylinder as well as for the full double-walled system yield reasonably good agreement with the experimental data. Therefore, the new EHB model is the first structural model for a cylindrical aggregate that gives evidence that transition bands (4) and (5) (Fig. 3b) are of excitonic nature.

Summary and conclusion

We have studied an artificial light-harvesting model system that comprises two well-defined, multichromophoric subsystems in close proximity. This model system reflects the complexity of nature's highly efficient light-harvesting systems, which contain a hierarchy of coupled architectures. We map the electronic excitations onto the supramolecular structure and also probe the degree of interactions between the two subsystems. Two complementary experimental approaches were used: controlled oxidation chemistry and flash dilution, both used in combination with linear absorption spectroscopy. We experimentally isolated the absorption spectrum of a single cylindrical dye aggregate, which is a building block for the coupled assembly, effectively electronically uncoupling it from the assembly while keeping the morphological structure intact. Extracting the uncoupled properties of an individual building block was crucial in developing a new theoretical understanding both of the microscopic structure of the assembly of the dyes forming the individual cylinders, and of how this structure determines the optical properties of the higher-order assembly.

Our results unambiguously demonstrate that our supramolecular model system is composed of two separate excitonic subsystems that are electronically weakly coupled. These findings are crucial for reducing the complexity of light-harvesting model systems and understanding to what extent multichromophoric systems in close proximity share their excitonic transitions. Previously, time-resolved nonlinear spectroscopy experiments, such as pump-probe^{33,34} and two-dimensional electronic spectroscopy^{38–42} on similar artificial model systems, suggested conflicting results. The current work demonstrates how it is important to have a detailed understanding of the linear spectrum to further interpret the nonlinear spectroscopy. We show that oxidation chemistry can be used as an elegant and convenient tool to reduce the complexity of

multichromophoric systems so as to unravel the supramolecular origin of their exciton transitions. The presented results yield better insight into the excitonic coupling within multichromophoric nanoscale systems. These results lead towards a fundamental understanding of what properties control the energy transport processes within and between such systems, which is vital for new developments in artificial light-harvesting and optoelectronic applications.

Methods

Preparation of light-harvesting nanotubes. The amphiphilic cyanine dye derivative 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-diocylbenzimidacarbocyanine (C8S3, $M_w = 902.8 \text{ g mol}^{-1}$, Fig. 1a) was obtained as a sodium salt (FEW Chemicals) and used as received. The light-harvesting nanotubes, consisting of double-walled nanotubular dye aggregates, were prepared in water/methanol starting preparing a 2.92 mM stock solution C8S3 powder in pure methanol (Fisher Scientific). A volume of 130 μl of the C8S3 stock solution was added to 500 μl of ultrapure H_2O , slightly shaking by hand to ensure even mixing. An immediate colour change from clear orange to deep pink was observed, indicating the formation of double-walled nanotubular C8S3 aggregates. The solution was stored in the dark for 24 h before adding an additional 500 μl of ultrapure H_2O to stabilize the aggregation process, resulting in a final dye concentration of $c_{\text{C8S3}} = 3.36 \times 10^{-4} \text{ mol l}^{-1}$. Solutions of light-harvesting nanotubes were stored in the dark and used for experiments within three days of preparation.

Chemical oxidation of light-harvesting nanotubes in solution. To a 400 μl nanotube solution was added 11 μl of 10 mM AgNO_3 solution. Absorption spectra were taken within 90 min of adding AgNO_3 .

Flash-dilution technique of light-harvesting nanotubes in solution. A flash-dilution technique was developed to preferentially alter the outer-wall cylinder of the double-walled light-harvesting nanotube. A water/methanol solution ($\sim 2 \text{ ml}$, equal concentration as in the neat nanotube solution) was placed into a 10 mm quartz cell while stirring the solution using a polytetrafluoroethylene (Teflon)-coated stir bar and magnetic stir plate. A small amount of the neat nanotube solution ($\sim 0.13 \text{ ml}$, $c_{\text{C8S3}} = 3 \times 10^{-4} \text{ mol l}^{-1}$) was abruptly added to the stirring water/methanol solution (to render a final dye concentration of $c_{\text{C8S3}} = 2 \times 10^{-5} \text{ mol l}^{-1}$). Before adding the nanotube solution to the water/methanol solution, the cell was taken off the stir plate. Absorption spectra were taken immediately after flash dilution and again within 1 h.

Absorption spectroscopy. Absorption spectra from the solution were taken with a double-beam UV-vis spectrometer (Shimadzu UV-2101PC) in a 0.2 mm demountable quartz cell (oxidation experiments) and a 10 mm quartz cell (flash-dilution experiments), both cells from Hellmar GmbH.

CryoTEM. As described in ref. 26, droplets of the solution (5 μl) were applied to perforated (hole diameter, 1 μm) carbon film covered 200-mesh grids (R1/4 batch of Quantifoil Micro Tools GmbH), which had been hydrophilized before use by simply storing the grids over a water bath for a day. Supernatant fluid was removed with filter paper until an ultrathin layer of the sample solution was obtained spanning the holes of the carbon film. The samples were immediately vitrified by propelling the grids into liquid ethane at its freezing point (90 K) with a guillotine-like plunging device. Frozen samples were transferred into a Philips CM12 TEM using a Gatan cryoholder and transfer station (Model 626, Gatan). Microscopy was carried out at a 94 K sample temperature using the microscope's low-dose protocol at a calibrated primary magnification of $\times 58,300$ and an accelerating voltage of 100 kV (LaB6-illumination). The defocus was chosen to be 1.2 μm to create sufficient phase contrast for imaging. Image analysis was performed with WaveMetrics software (IGOR Pro 6.0).

Singular value decomposition. SVD⁴³ was performed using Mathematica (version 8.01, Wolfram Research).

Theoretical calculations/modelling. The structural model for each cylindrical wall was obtained by rolling a lattice with two molecules per unit cell (described in the main text and Supplementary Sections S4 and S5) onto a cylindrical surface. Optical electronic excitations in each wall were described by a Frenkel exciton Hamiltonian that accounts for the electronic excitation energies of the molecules and the intermolecular transfer interactions determined by extended transition dipoles (Supplementary Section S4). The thus obtained Hamiltonian was diagonalized numerically, yielding the exciton eigenstates and allowing for the calculation of the optical spectra. As far as possible, the structural and electronic model parameters were taken from experiment or earlier results on cylindrical dye aggregates^{23,26,33,35}; the remaining parameters (three geometric angles per wall and several line widths) were fitted by comparing the eventually obtained absorption spectra with experiment (Supplementary Section S5).

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Author contributions

J.P.R., D.A.V.B., J.K. and D.M.E. developed the project. D.M.E. performed experiments and data analysis, put results into perspective, and initiated the collaborations. E.A.B., S.M.V. and C.v.d.K. designed the theoretical model with guidance from J.K. E.A.B. analysed the theoretical model and performed the fit to the experimental spectra, supervised by J.K. C.W.C. performed SVD analysis under the guidance of D.A.V.B. R.J.S. and M.G.B. provided helpful discussions and beneficial interpretation of the data analysis. D.M.E., E.A.B., S.M.V., J.K., M.G.B. and D.A.V.B. co-wrote the paper, with input from the other authors.

Additional information

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