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Quantum effects in biology

Chapter 16: Design and Applications of Bio-inspired Quantum Materials

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In this chapter we explore the opportunities that the dynamical quantum effects recently revealed as components of key functions of plants and higher organisms and described in previous chapters, might offer for design of new nano-scale materials possessing quantum-enhanced functionality. We discuss the potential applications for such biomimetic materials with engineered quantum properties, and present a review of progress thus far on two prototypical systems: biomimetic light harvesting materials and biomimetic magnetic sensors.

I. POTENTIAL APPLICATIONS OF BIO-INSPIRED QUANTUM MATERIALS

It is well appreciated that quantum dynamics can lead to enhanced performance in tasks such as metrology [1], computing [2], and communication [3]. However, such enhancements have yet to be realized for artificial systems in the biological domain. As discussed in earlier chapters of this book it has been demonstrated or hypothesized that quantum processes are critical to the accurate description of the functional dynamics of several biological systems. What opportunities do these observations present for the motivation and development of biomimetic materials? The possibility of constructing artificial materials with the ability to mimic natural systems leads to a diverse range of potential applications. A key question is thus whether we can use nature's ingenuity as inspiration and incorporate quantum effects into synthetic systems to provide quantum enhanced function? Such explorations also hold out the tandem promise of achieving greater understanding of the role of quantum mechanics in biological function, since in contrast to the traditional top-down approach to investigating natural systems, this perspective requires the development of a bottom-up approach to synthesis of unnatural systems possessing capability to mimic all or part of some biological role.

Several intriguing possible directions for such applications arise from the developments in understanding how quantum effects affect the dynamics of biological phenomena described in earlier chapters. These include several sensing applications, e.g., of single molecules, of light or of weak magnetic fields, as well as the synthesis of robust, fault forgiving devices for energy transfer, and smart pixels controlled by dendrimer states for imaging [4]. In what follows we focus on the opportunities presented by artificial light harvesting systems and radical pair materials for sensing of light and magnetic fields, respectively. We describe here the motivations for these two directions, as well as candidate architectures and challenges to be overcome in order to be able to realize such applications.

A. Opportunities for novel energy and sensing applications with artificial light harvesting systems

As we have seen in earlier chapters of this book, natural light harvesting systems are both highly complex in structure and highly specialized in function. Taken together with the recent observations of quantum coherences in the dynamics of electronic energy transport through these biological units, these features raise several intriguing questions. On the one hand, it prompts us to ask whether the coherent quantum dynamics associated with energy transport in these systems are the result of a finely tuned evolutionary process that has maintained and even refined the excitonic coherence in the face of mounting structural complexity in order to enhance light harvesting? Or are these manifestations of coherent quantum dynamics merely a by-product of structural evolution that is driven by quite different adaptive pressures or even just by response to genetic drift? Looking backwards for answers to the biological origin of coherence in natural systems constitutes a major question that will require a significant interdisciplinary effort between biology, physics and chemistry to make progress. Quite a different set of questions is generated if we look forwards from the natural light harvesting systems prevalent in biology today and ask "what can we do with artificial light harvesting systems that are designed to emulate one or all functions of the natural systems"?

We can envisage artificial light harvesting systems that range from complete biomimetic structures, to systems that either emulate just one feature of the natural systems or translate some natural function to a different, unnatural regime. Given the possibility that natural structures have been optimized by aeons of evolutionary development, development of functionally specialized artificial systems appears more realistic and also more straightforward. The growth of supramolecular chemistry and self-assembly methods over the last twenty years allows us to consider a wide variety of structures as viable platforms for such artificial light harvesting systems. A key question is then, what are the revolutionary applications that become possible with such biomimetic systems?

One immediate application is robust, high efficiency solar energy conversion. Such a goal of achieving a complete biomimetic of natural photosynthetic systems is clearly a major and high-profile application for our society today, given the need to find alternative energy sources to fossil fuels. Significant research efforts are going into solar cells and a wide variety of solid state photovoltaic [5] and thin film, solid-liquid photoelectrochemical cells [6] are under development. Artificial light harvesting arrays consisting of organized assemblies of chromophores and proteins constitute an alternative to conventional solar cell technologies [7]. Within the general framework of tailored environments for light harvesting achieved by molecular self-assembly, the role of quantum coherence in facilitating energy transport through complex pigment-protein structures can provide an additional “knob” with which to tune the supramolecular level design of functional artificial light harvesting complexes. This capability can be explored by systematic, “bottom-up” studies of pigment-protein complexes with controllable inter-pigment distances and relative orientation, which determine the coupling between chromophores and are hence a primary factor in the extent of quantum coherence. However, when used as an energy source, such artificial systems also require the incorporation of catalysts that facilitate the charge separation and redox chemical reaction steps of photosynthesis [8]. Whether this is realized as an integral part of the self-assembled structure, or whether the light harvesting array is integrated within a solid-state device, the scale up from light harvesting to a fully functional photosynthetic unit that produces chemical energy from sunlight is extremely challenging.

More diverse opportunities are presented when attention is focused only on mimicking the light harvesting functionality of a synthetic pigment-protein complex, without also incorporating the additional requirements of a complete photosynthetic biomimetic system. One promising direction is to build on the exquisite ability of some light harvesting antenna systems to collect light and function under very low intensity conditions. For example, green sulfur bacteria are able to harvest light deep in the Black Sea under conditions corresponding to 1 photon incident every 8 hours [9]. This suggests that an artificial light harvesting apparatus might provide an ultra-high performance photon sensor. Natural systems are effective at harvesting light in the optical and near infrared. While advanced technology for low intensity light detection already exists in these regimes, a biomimetic light harvesting photon detector would offer several unique capabilities. These potentially include customizability and versatility, low weight, low cost, the ability to operate at room temperatures with high quantum efficiency, and the ability to respond to a broad band of photon wavelengths. Such artificial structures can in principle also be tailored for sensitivity deeper into the infrared. Indeed, such a biomimetic device would be of greatest interest if it could operate over a broad range of infra-red wavelengths, where single photon detection tools are currently extremely restricted.

Although there have been previous efforts to integrate natural light harvesting structures into solid-state environments for photodetection, there have so far been no systematic efforts to mimic light harvesting structures and take advantage of their quantum coherent properties in order to create sensitive light sensors. The use of biomimetic synthetic structures possesses additional advantages over the simple integration of natural photosynthetic complexes. For example, the constraints of device integration severely restricts the list of possible candidate natural light harvesting arrays, yet synthetic supramolecular arrays present a vastly larger landscape of possibilities. Furthermore, given our rapidly increasing understanding of the relation between excitonic quantum coherence and structural features of light harvesting arrays, we can now begin to tune the properties of synthetic arrays as desired to optimize performance of light sensing. The protein scaffolds of viruses provide one attractive option for synthetic design of such artificial systems, both on account of their highly ordered structures and because of the ability to generate a range of well-defined structures by self-assembly under unnatural conditions. Such systems also possess the potential for attachment to electroactive surfaces via electron transfer functional groups, which would enable the energy collected by the light harvesting system to initiate electron transfer, thereby allowing electrical detection of the incident photon. Progress in constructing such protein-scaffolded light harvesting antennas will be reviewed in the next section.

The end goal of this research is to produce robust photovoltaic or light sensing technologies with control over the nanoscale structure. Manipulating this structure allows tuning of light capture, energy transfer, and free-carrier generation processes; engineering of these processes is expected to allow improvements in some combination of: quantum efficiency, utilized solar spectrum, sensitivity to specific wavelengths, durability, or production costs.

B. Magnetic sensing with radical pair materials

During great migrations birds navigate by detecting the inclination of the Earth’s magnetic field, which varies predictably with latitude [10]. As discussed in Chapter 11 of this book, one hypothesis for exactly how birds sense the Earth’s magnetic field is that they exploit quantum mechanical evolution of photo-excited radical pairs. Although a definitive experimental confirmation of this radical pair mechanism in bird navigation is still outstanding, this hypothesis has inspired researchers to consider artificial devices for magnetometry based on radical pair reactions (see also Ref. [11]).

Magnetometry is a well-developed field, and there exist many commercial magnetic field sensing devices based on

diverse physical phenomena. Sensing magnetic fields is in fact a critical component of many everyday technologies, including airplanes, navigation tools, and medical diagnostic tools. See Ref. [12] for a review of modern magnetometry methods and technologies. The most sensitive detector of a DC, or low frequency, magnetic field is the SQUID magnetometer which can detect fields of order 10^{-14} Tesla (T). Magnetometry is also a field where quantum mechanical effects have been exploited to increase sensitivity – e.g., the Josephson effect underlies SQUID magnetometers, while nanoscale magnetometers reliant on manipulating spin coherence have recently been constructed using color centers in diamond [13, 14]. A useful distinction to bear in mind is that there are two types of magnetic field sensing tasks: one, the sensing of the overall magnitude of a magnetic field, and two, the sensing of the vector components of a magnetic field. The latter task, that of sensing a field direction is typically a more difficult one.

What is the motivation for building a biomimetic magnetic field sensor – a *chemical compass* – based on the radical pair mechanism? ¹ Given the remarkable sensitivities of modern magnetometers [12] it would be quite ambitious to suppose that a biomimetic magnetic field sensor could match these standards. However, there are factors other than sensitivity that dictate the utility of a magnetic sensing device, including: cost of production, cost of maintenance, operating temperature, frequency response, stability, reliability, size, and power requirements. Although the development of sensor based on the radical pair mechanism is still nascent, the hope is that such a sensor will be superior in some of the above measures of utility. Specifically, it is very plausible that a radical-pair-based magnetic field sensor constructed from organic components will have lower production costs and lower power requirements, and have higher operating temperatures than many of today’s commercial magnetometers.

II. PROGRESS ON DESIGNING BIOMIMETIC QUANTUM MATERIALS

Having provided an overview of the motivation and challenges in the field of biomimetic quantum-enhanced material design we now present a review of progress made thus far on the design and synthesis of such materials.

A. Structured chromophoric assemblies for light harvesting

Every one of Nature’s light harvesting complexes (LHCs) is at its core an assembly of light absorbing pigments. The wondrous aspect is how such assemblies are accurately and reliably constructed from basic building blocks such as molecules from the chlorophyll, carotenoid, or porphyrin families, with protein structures providing scaffolding when necessary. Particularly remarkable are the photo-stability of natural light harvesting antennas and the mechanisms involved in *photo-protection*, the range of defense mechanisms by which LHCs regulate energy absorption and transfer to prevent oxidation damage, e.g. see Ref. [15]. In fact, current organic photovoltaics are sorely lacking such photo-stability and regulatory processes, and this is one of the primary obstacles to their commercial success [16].

Over the past two decades much effort has been invested in producing artificial light harvesting units that mimic the structure and properties of natural LHCs. The aspect that distinguishes these efforts from organic photovoltaic devices based on polymers (section 16.1) or quantum dots (section 16.2) is the driving force of their biomimicry as well as their attempts to use the same, or similar, building blocks seen in Nature. This sometimes results in directly integrating entire sections of natural LHCs with an inorganic device framework. There are at least three specific properties that such biomimetic artificial light harvesting or light sensing devices strive to replicate from the model of natural light harvesting complexes:

1. A near unit efficiency of energy transfer from the region of light absorption to the region of charge separation where the exciton that results from light absorption is converted into a charge separated electron and hole.
2. A near unit efficiency of charge separation that occurs at the reaction center in natural light harvesting complexes.
3. The above mentioned photo-stability and photoprotection mechanisms of natural light harvesting complexes.

To date, no biomimetic approach has been successful in replicating all of the above properties in a single device. This is perhaps not surprising, since replicating the performance of natural LHCs is a formidable task. The initial steps of light capture and conversion involve fragile excited states and charge-separated states that are vulnerable to numerous reactions that dissipate the captured energy as wasted heat. Precise control over nanoscale structure

¹ We use the term “biomimetic” somewhat loosely here since to date it has not been proven that the radical pair mechanism underlies bird navigation.

is needed to regulate and inhibit these dissipation channels, and this is one of the great challenges for the fields of synthetic and supramolecular chemistry. Ideally, one would like to construct an artificial light harvesting complex from the molecular level up. However, present – covalent or supramolecular – synthesis techniques, advanced as they are, are not quite at the stage where one can both tailor nanoscale structure and at the same time produce large-scale molecular arrays.

In this section we will review some of the demonstrated techniques, as well as some promising proposals, for constructing biomimetic light harvesting antennas for photovoltaic or light sensing applications.

1. Direct integration of natural antennas into solid-state environments

The most obvious way to leverage the superior light capture and conversion capabilities of natural LHCs, is to directly “wire up” such structures to a charge collection device that extracts the electrons produced by charge separation. These electrons then constitute the detection signal for light sensors or the electrical current in a photovoltaic. Of course this approach has the potential to preserve all the quantum properties of the natural LHC that is integrated, but great care must be taken to ensure that the functioning of the LHC is not adversely effected by integration into an extremely foreign solid-state environment.

Such an integration of a natural light harvesting complex and a solid-state electron collection device has been accomplished by the Baldo group at M.I.T. [17] (see also Ref. [18] for a supporting study). This group has integrated two biological LHC components, the reaction center (RC) from the purple bacterium species *Rhodobacter sphaeroides* and Photosystem I (PSI) from spinach, into solid-state electronic devices. See Figure 1 for a cross-section of the constructed device. The challenge of preserving light harvesting functionality of the biological complexes within the solid-state environment was overcome by careful design of the assembly process. The molecular complexes were self-assembled on a gold-coated surface which was functionalized with an affinity resin to immobilize and orient the pigment-proteins. Then the complexes were stabilized using customized peptide surfactants. This self-assembled layer was finally covered with an amorphous organic semiconductor before deposition of top metal contacts for collection of the generated charges. The authors of the study stress that the use of custom peptide surfactants and the organic semiconductor layer between the photosynthetic complexes and the metal contacts were absolutely crucial for preserving the functionality of the RC and PSI units.

FIG. 1: A cross section of the device integration of reaction centers from Ref. [17]. Figure provided courtesy of Prof. Marc Baldo, M.I.T.

The study measured the photocurrent generated in the RC and PSI integrated devices and confirmed that its excitation wavelength dependence matches the solution phase absorption spectra of the respective light harvesting complexes. This is a good indication that the functionality of the complexes was preserved during the integration process and that they were functioning as light harvesting modules of the device. In addition, the authors estimate that the internal quantum efficiency of the device is 12% and predict that it could be increased to 20% by improvements in the integration process. However, it should be noted that there is another limiting factor for such devices: the self-assembled light harvesting components (RC or PSI) absorb very little of the available light ($< 1\%$) because they form a thin monolayer. This leads to low overall power efficiencies and has to be overcome before such devices can be considered true photovoltaics. Related recent experiments on biohybrid device development have focused on use of the chlorosome of green sulfur bacteria (see below), which offers greater light absorbance. Encouraging results have been obtained using both columnar structures of the chlorosome formed by electrospray-deposition onto dye-coated TiO_2 surfaces [19] and chlorosomes that were weakly associated with graphite electrodes [20].

In addition to the above experiments measuring optoelectronic energy transfer, several studies have focused on the controlled placement and immobilization of biological light harvesting complexes onto solid surfaces. These studies achieve the immobilization, control over orientation, and patterning of LHCs by complex surface lithography and chemical functionalization techniques which show potential for tailoring nanoscale structure of biological LHCs adsorbed onto surfaces. Similar to Ref. [17], the most commonly used technique is to form self-assembled monolayers on gold or glass substrates, and then to selectively chemically modify (e.g. CH_3 -terminate) parts of these monolayers so that they resist or attract adsorption by LHC proteins. The resolution at which this chemical modification can be done determines the length scales at which the patterning of LHCs can be achieved. This technique was utilized by Ciobanu *et al.* to immobilize PSI complexes [21], by Reynolds *et al.* [22] to immobilize LH2 complexes from purple bacteria, and by Escalante *et al.* [23] to immobilize LH1 and LH2 complexes from purple bacteria. Microscopy was used in these studies to confirm the patterned adsorption of light harvesting complexes onto a surface, and Reynolds *et al.* and Escalante *et al.* also used fluorescence spectroscopy to confirm that the optical properties of the LHCs were not significantly modified (compared to solution phase spectra) by adsorption onto the surface. From this retention of optical properties they conclude that the structure integrity of the LHCs is preserved through the adsorption and patterning processes. However, it should be noted that in contrast to the Das *et al.* study discussed above, these adsorption studies did not have a scheme to collect photocurrents and therefore demonstrate photovoltaic functionality.

The experiments detailed in this section, especially that in Ref. [17], are promising demonstrations of an approach to construct devices that can leverage the excellent light capture and exciton transport performance of biological light harvesting complexes. However in the context of this book, one must ask whether the quantum properties of the light harvesting components (RC, PSI, LH1, and LH2) were preserved during the integration process, and still present in the final devices. The matching of solution phase absorption spectra by device photocurrents in Ref. [17], and a similar matching of fluorescence spectra of surface adsorbed samples to solution spectra in Refs. [22, 23], are encouraging evidence that the structure and hence excited state dynamics of the photosynthetic pigments were largely preserved. However, it is impossible to conclude at this stage whether the excitonic properties and energy transfer properties were unaltered (or enhanced). Further experiments examining energy transfer in the integrated photosynthetic complexes will be necessary for determining this.

2. Molecular aggregates

The term molecular aggregate is commonly reserved for densely packed molecular structures (Figure 2(a)) that result from non-covalent intermolecular interactions such as pi-pi stacking, hydrogen bonding, and metal ion coordination: so-called supramolecular assemblies. Such interactions can lead to both extremely regular organization of constituent molecules-molecular crystals-and also less regular, disordered arrangements. Studies on molecular aggregates in the early 1930s revealed that the optical properties of solutions of some organic dyes change drastically upon changing their dye concentration [24–29]; it was found that upon increasing the concentration of pseudo-iso-cyanine (PIC) dye in solution, the absorption spectrum changed such that the broad absorption band at a wavelength of ~ 525 nm disappeared and was replaced by a narrow absorption band at a wavelength of 570 nm. Because this effect was first discovered independently by Jelley and Scheibe such a new, narrowed, and red-shifted absorption band (Figure 2(b)) is now generally known as the J (Jelley) band or the S (Scheibe) band. This new absorption band, the J-or S-band, is associated with extended electronic excitations of aggregated PIC molecules [30], much like the well-known Frenkel excitons of molecular bulk crystals [31]. Molecular aggregates with such new, narrowed and red-shifted absorption bands are therefore referred to as J-aggregates (or, less commonly, as S-aggregates).

In the past, such J-aggregates have found significant applications in the field of photography where they are used to increase spectral sensitivity of films. More recently, molecular aggregation has been recognized as a useful framework for describing, and imitating, many natural photosynthetic light-harvesting complexes [32]. The techniques and language used for describing the molecular aggregates found in these natural light-harvesting systems is exactly the same as those applied to molecular J-aggregates, which caused a rapid merging of these two fields. The increasing interest in J-aggregates is mainly due to their unique collective optical properties, whereby the optical response of the aggregated dye molecules is fundamentally different from the addition of the optical response of the individual dye molecules. This behavior results from the collective Frenkel excitons that describe the excited states of the aggregates.

Perhaps nature’s most efficient light harvesting antenna system is the *chlorosome* antenna of green sulfur bacteria, one of only few phototropic organisms that can survive by photosynthesis in the extremely light-sparse environment of deep sea [33–35]. Typically these bacteria live in conditions with very little light and hence their light capture apparatus has to be extremely effective at absorbing the available light and transporting resulting photo-excitations to reactions centers. The chlorosome antennas are almost 100% efficient at these tasks. In contrast to many other antenna structures, especially those in higher plants, the chlorosome consists solely of pigment molecules (bacteriochlorophyll

FIG. 2: Aggregation of cyanine dye molecules. (a) Schematic illustrating the closely packed molecules within molecular aggregates via non-covalent intermolecular interactions such as pi-pi stacking; (b) Absorption spectra of cyanine dye derivative (TDBC) in solution: low concentration (black line) and at high concentration (red line); upon increasing the dye concentration dramatically the molecules aggregate to form J-aggregates. [Adapted from: D.M. Eisele “Optical, Structural and Redox Properties of Nanotubular J-aggregates of Amphiphilic Cyanine Dyes.” Aachen. Shaker Verlag (2010) ISBN 978-3-8322-9120-4]

c, *d* and *e*), with no protein scaffolding. The unique ability of the chlorosome to harvest and transport energy efficiently derives from the closely packed aggregates of pi-conjugated molecules that constitute the supramolecular assembly [35]. Although the details of the molecular packing on the atomic level are still under debate [36–40], recent studies propose that these highly efficient antennas consist of cylindrical aggregates (Figure 3) with a diameter of the order of 10 nm and lengths that may extend to several hundred nanometers, containing several hundred thousand bacteriochlorophyll molecules. [35].

Partly motivated by the desirable performance of Nature’s light harvesting molecular aggregates, several researchers have attempted to synthesize customized molecular aggregates for light harvesting and solar energy technologies. The first challenge with this approach for producing artificial light harvesting antennas is that it is essential to have a theoretical understanding of how aggregate structure influences the optical and energy transfer properties crucial to light harvesting. It is clear from the close proximity of pigments in typical molecular aggregates that quantum properties will be relevant to both optical properties and energy transfer. At separation distances $\lesssim 4$ nm it is important to describe the electronic coupling between pigments in detail and fully quantum mechanically. The distribution and orientation of exciton dipoles which can only be understood when the coupled system is modeled quantum mechanically, dictates optical properties such as absorption (see Box 1). Furthermore, the formation, extent of delocalization and transport of excitons governs how efficient the aggregate is at transferring energy from where the light energy is absorbed where it is eventually used (typically charge separation interfaces). These effects can only be described by a quantum mechanical model and not a semi-classical one such as Förster energy transfer theory (see chapter 4), and such descriptions can be complex.

The second challenge with the molecular aggregate approach is that one must gain enough experimental control over the aggregation process so that the final product can be manipulated to have desirable light capture and energy transfer properties. Typically such aggregates are produced by a solution-based self-assembly processes, and the final morphology of an aggregate is dependent on many factors including: the species and concentration of the constituent molecules, temperature, and solvent properties such as pH. Hence there are many control “knobs” in the assembly process and part of the relatively new field of supramolecular chemistry [41] is concerned with understanding how each of these influences structure and morphology.

Despite these challenges many attempts have been made to produce synthetic molecular aggregates for light harvesting with a multitude of constituent pigment molecules. The extraordinary chlorosome antenna system has inspired much work on cylindrical supramolecular systems that self-assemble from various artificial pi-conjugated molecules that can interact with light, *e.g.* porphyrin derivatives [43], hexabenzocoronene derivatives [44], or naphthalenetetracarboxylic acid diimide derivatives [45]. Also notable are ambitious attempts to self-assemble large supramolecular structures having several covalent building blocks that each function as some component of an artificial light harvesting complex [46]. As a representative survey of the large variety of pigments that have been used to form molecular aggregates for potential light harvesting applications, we will describe here the most common examples, which are the families of (a) cyanine, of (b) Zinc chlorin, and of (c) phorphyrine based pigments.

FIG. 3: Proposed schematic structure of the chlorosome antenna of green sulfur bacteria. Left panel shows the location of several chlorosomes (green) within the antenna, the Fenna-Matthew-Olson complex located within the membrane (yellow) and the reaction center below the membrane. Middle panel shows a rendition of the cylindrical structure of individual chlorosomes (

. The right panel shows the proposed packing of bacteriochlorophyll molecules within a chlorosome [42].

(a) *Cyanine dyes and amphiphilic derivatives*. Even before their discovery by Jelley and Scheibe in the early 1930s, the cyanine dye derivatives had long been recognized as important spectral sensitizers for photographic imaging [47] and nonlinear optics applications, on account of (1) their extraordinarily sharp absorption bands arising from the large, highly delocalized pi-conjugated systems, and (2) their unique aggregation properties. They are also well established as model systems for studies of photo-activated electron transport processes using monolayer assemblies at solid state and liquid interfaces [44, 48]. When cyanine dyes are dispersed in polar solvents above a critical concentration level (usually low mM), they self-assemble into molecular aggregates. Although the unique properties of cyanine dye J-aggregates, such as their highly efficient energy transfer properties, have been realized for decades [49], most recently they have received attention for use in artificial LHCs. In particular, amphiphilic cyanine dye derivatives can be used to generate structures similar to the cylindrical chromosomes of photosynthetic green sulfur bacteria. Consequently, artificial light harvesting antennas composed of cyanine dye J-aggregates that mimic natural systems have been proposed [49]. Optical and energy transfer properties can vary widely based on the aggregates morphology and the details of the spatial arrangement of molecules within the aggregate; it is well known that both parameters are controlled by the chemical structure and functional groups of the particular cyanine dye.

An entire new class of cyanine dye derivatives was synthesized in the early 1990s by Siegfried Dähne and co-workers. They synthesized a library of amphiphilic cyanine dye molecules by adding various hydrophilic and hydrophobic functional groups to a cyanine dye molecule [50, 51]. One example of these molecules, abbreviated as C8S3, is shown in Figure 4(a); when dissolved in a polar solvent these molecules self-assemble due to superposition of hydrophobic forces (of the amphiphilic side chains) and the pi-pi stacking (of the chromophores) into double-walled nanotubular J-aggregate structures consisting of two concentric cylindrical dye aggregates in an artificial light-harvesting nanotube (Figure 4(b)) [52].

The optical properties of individual C8S3 light-harvesting nanotubes (Figure 4) investigated by means of polarization-resolved fluorescence Near-field Scanning Optical Microscopy (NSOM) revealed that their supramolecular structure is highly uniform both along an individual tube and between different tubes within an ensemble [53]. This makes them an excellent model system for fundamental investigations of exciton transport in individual quasi-one-dimensional nanostructures as well as for light harvesting and other optoelectronic applications in future solid-state devices. Most importantly, it allows for studying the properties of the individual nanotube by investigating the ensemble in a solution sample. However, in order to control such large supramolecular systems it is essential to understand both how their various parts interact with each other and also whether these interactions result in coherently shared excited states (excitons) or in diffusive energy transport between them. Through selective chemistry it was possible to unambiguously determine the supramolecular origin of the excitonic transitions in the nanotubes (Figure 4c). Furthermore, it was found that the two cylinders of the nanotube, while being only ~ 4 nm apart from each other, have distinct spectral responses and are best described as two separate, at most

weakly coupled excitonic systems [54]. Understanding such interactions is critical to the control of energy transfer on a molecular scale, a goal for diverse applications ranging from artificial photosynthesis to molecular electronics. Obtaining a detailed understanding of the linear spectrum of the aggregates is also a key step towards developing a fundamental understanding of how the details of the supramolecular structure influence the optical and energy transfer properties that are critical for light harvesting.

FIG. 4: Light-harvesting nanotube consisting of double-walled cylindrical aggregates of amphiphilic cyanine dye molecules. (a) Amphiphilic 3,3-bis(2-sulphopropyl)-5,5,6,6-tetrachloro-1,1'-dioctylbenzimidacarbocyanine (C8S3) monomer [50]. (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 nanotube has a diameter of about 13 nm and is several μm in length. The distance between the two concentric cylindrical aggregates of about 4 nm [55]. (c) Absorption spectra. Black: dye monomers dissolved in methanol (no aggregation). Red: nanotubular dye aggregates prepared in water/methanol; the two main J-bands can be unambiguously assigned to inner-wall and outer-wall cylinder, respectively [54].

- (b) *Zinc chlorin and its derivatives.* ZnChl is very similar to BChl *c* in form, with the Mg metal center of BChl *c* being replaced by Zn. It has been shown that derivatives of ZnChl self-assemble into nanoscale rods similar to the chlorosome (e.g. [56]). In fact, some such aggregates have spectroscopic properties that closely match those of natural chlorosomes [57]. Furthermore, using time-resolved fluorescence it was determined that excitons are delocalized among at least 10-15 molecules and that exciton transport timescales are of 1-10 ps [58]. Thus it would seem that the quantum properties of such aggregates are important, as would be expected from the large density of pigments and their similarity to the chlorosome. More recently, such ZnChl aggregates have been appended with other organic components (in a self-assembling manner not requiring the assistance of structure stabilizing proteins) to enhance their capabilities. Katterle *et al.* formed a co-aggregate of ZnChl and BChl which is covalently linked to a C60 molecule [59]. This combined self-assembling structure functions as a complete “light harvesting unit” with the ZnChl aggregate functioning as a light collection antenna, the C60 as an artificial reaction center performing charge separation, and the intermediary BChl functioning simultaneously as an energy trap for the ZnChl antenna and an electron donor for the C60 reaction center. This combined structure achieves very fast energy transfer and charge separation and an overall quantum efficiency of 90%. Another modification of ZnChl aggregates was performed by Röger *et al.*, who appended additional peripheral pigments to the tubular structure in order to harvest the green and orange portion of natural sunlight [60, 61]. This modification was shown to increase harvesting efficiency by 63% (as compared to the bare ZnChl aggregate) by enhancing spectral coverage.
- (c) *Porphyrin based dyes.* Porphyrin based dyes are another family from which aggregates are commonly built for light harvesting functionality. Perhaps the most studied aggregates from the porphyrin family are the self-assembling nanoscale rods formed from the Tetrakis(4-sulfonatophenyl)-porphyrin (TPPS₄) derivative (e.g. Ref. [62]). Spectroscopic studies suggest that excitons in the TPPS₄ aggregate are initially delocalized over ~ 10 molecules but then rapidly become more localized to one or two molecules [63]. The Shelnutt group has also constructed several aggregates of porphyrin derivatives that are unique in that they utilize the supramolecular technique of ionic self-assembly [64] for aggregation. This enables the synthesis of a variety of aggregate morphologies with multiple constituent monomer porphyrins. Structures synthesized including tubular aggregates with a mixture of two porphyrin derivatives [65], and clover-leaf shaped dendritic structures composed of two types of metallic porphyrins

[66]. The latter are particularly intriguing because the authors of that work show that it is possible to change the electronic character of the constituent molecules without affecting the morphology. This allow one to tune electronic properties of the binary solid (from photoconductor to insulator for example) by altering the metal ions of the constituent porphyrins. Inter-molecular distances suggest that quantum effects will be important for describing optical and energy transfer properties in these porphyrin aggregates, however no spectroscopic data is available for them to date.

Finally, it is important to note that at this stage, unlike the development of prototype biohybrid devices with natural light harvesting systems described above, none of these supramolecular aggregates have been integrated into a device with photovoltaic capability. Such integration and the stability of the molecular aggregates during it will be crucial to the viability of this approach to artificial light harvesting.

Box 1: Optical properties of molecular aggregates

Inter-molecular separation in molecular aggregates is in the range 0.4–2nm, with smaller distances being typical in synthetic dye aggregates such as the classic molecular aggregate pseudoisocyanine chloride (PIC), and larger distances being more prevalent in molecular aggregates found in nature such as the LH2 complex of purple bacteria. At these separation distances the electronic interaction between two pigments is primarily Coulombic (i.e. exchange and other short-range interactions are negligible) [67]. Furthermore, it is common to use a point-dipole approximation for the Coulomb interaction. Within this approximation, the redistribution of charge that results from molecular excitation is represented by a single transition dipole moment, $\vec{\mu}$, and interaction between molecules is modeled by a dipole-dipole interaction between these transition dipoles. This approximation to a full Coulomb integral is appropriate if the intermolecular separation is larger than the physical extent of both molecules. If this condition does not hold then higher order expansions of the Coulomb integral – multipole expansions – should be employed.

Within the dipole approximation, the interaction between two neighboring pigments is:

$$V(r, \mu_1, \mu_2) = \frac{1}{4\pi\epsilon_0} \left(\frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r})}{r^3} \right) = \frac{|\mu_1||\mu_2|}{4\pi\epsilon_0 r^3} (-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi) \quad (1)$$

where ϵ_0 is the permittivity of free space, $\vec{r}$ is the vector between the two molecules and $\hat{r}$ is its normalized version (i.e. $\vec{r} = r\hat{r}$). The angles used in the second form of the coupling are the angles between the dipoles and the vector separating them (see figure below).

Consider a transition from the singlet electronic ground state of a molecule, $|S_0\rangle$, to a singlet excited state, $|S_1\rangle$, separated in energy by ϵ . Once excited, the two molecules will interact and the Hamiltonian describing this interaction (under the Heitler-London approximation which is appropriate when $\epsilon \gg V$) is:

$$\mathcal{H} = \epsilon_1 |S_1^{(1)}\rangle \langle S_1^{(1)}| + \epsilon_2 |S_1^{(2)}\rangle \langle S_1^{(2)}| + V \left(|S_1^{(1)}\rangle \langle S_0^{(2)}| + |S_0^{(1)}\rangle \langle S_1^{(2)}| \right) \quad (2)$$

where the superscript indexes molecule number, and we have allowed the excited states of the two molecules to have different energies (due to local environment shifts or if the molecules are two different species). We have set the energy of the ground state of both molecules to zero for convenience and we are not describing any excited states with greater energy because it is only these states that dictate the linear optical properties which we are interested in. Diagonalizing this Hamiltonian yields new excited states ($|E_1\rangle, |E_2\rangle$) that have some contribution from $|S_1^{(1)}\rangle$ and $|S_1^{(2)}\rangle$: $|E_{1/2}\rangle = \alpha_{1/2} |S_1^{(1)}\rangle + \beta_{1/2} |S_1^{(2)}\rangle$.

Since the wavelength of light absorbed by such molecules is much larger than the inter-molecule separation, r , the light interacts with the combined dipole operator $\vec{D} = \vec{\mu}_1 + \vec{\mu}_2$. Then the light absorbed will be concentrated around the frequencies $e_1/\hbar$ and $e_2/\hbar$, and the magnitude of the absorption profile at these frequencies is proportional to $M_1 \equiv |\langle E_1 | D | G \rangle|^2$ and $M_2 \equiv |\langle E_2 | D | G \rangle|^2$, respectively, where $|G\rangle = |S_0^{(1)}\rangle \otimes |S_0^{(2)}\rangle$ is the ground state. It is interesting

is look at how these features of the absorption profile change with the structural details of aggregation. Obviously, as the distance between the chromophores increases their coupling decreases ($V \rightarrow 0$) and hence the absorption profile approaches the monomer absorption profile. The dependence on the angles defining the aggregate structure is less trivial, and in the following figures we show how the quantities e_1, e_2, M_1, M_2 change with the structural angles. For this example, we assume that the magnitude of both monomer dipoles is the same ($|\mu_1| = |\mu_2| = |\mu| = 10$ Debye), $\varepsilon_1 = 12,000\text{cm}^{-1}$, $\varepsilon_2 = 12,200\text{cm}^{-1}$, and $r = 15\text{\AA}$. Finally, for simplicity we will fix $\theta_1 = \pi/4$ and look at the dependence on the other two free angles.

There are several things to note from these surfaces. Firstly, the transition energies of the two excitons (eigenstates of $\mathcal{H}$) can be greater, or less, than the original monomer transition energies depending on the dipole angles. Also, from the plots of $M_{1/2}$ we see that the magnitude of the combined dipole is distributed across the two excitonic states. Depending on the values of the angles, either the lower eigenstate or the upper eigenstate can have the dominant dipole strength. This is an example of how the underlying structure strongly influences the optical properties of the aggregate. This redistribution of dipole strength (or oscillator strength) is a key feature of molecular aggregation, and can lead to striking features in linear spectra. For example, in the symmetric case where $\varepsilon_1 = \varepsilon_2$, and the dipoles are lined up head-to-tail (i.e. $\phi = \theta_1 = \theta_2 = 0$), *all* the dipole strength will be concentrated on the low energy exciton, and $M_2 = 0$. Large aggregates with this structure are known as *J*-aggregates [57], and this concentration of oscillator strength leads to a dominant narrow peak in their absorption spectrum.

3. Virus-templated chromophore assemblies

As we saw in the last section, a major challenge in utilizing biologically inspired molecular aggregates for light harvesting is controlling their nanoscale structure and morphology. A variety of non-covalent interactions must be controlled and precisely utilized to synthesize well-structured aggregates and the field of supramolecular chemistry is tackling this challenge. An alternative approach to overcoming this challenge is to turn to another one of Nature's marvelous processes: protein self-assembly. Self-assembly is a ubiquitous process in biology taking place at all length scales, from molecular to organismic [68]. Many of the synthetic molecular aggregates discussed in the last section are constructed using molecular self-assembly, but the self-assembling process occurs are larger lengths scales as well. In particular individual protein subunits often self-assemble into aggregate structures with a wide range of structural motifs (sheets, ribbons, helices). Some of the best understood protein self-assembly processes occur in viruses where *viral capsids*, protein shells that enclose and protect the genetic material of the virus, self assemble into a variety of shapes. Recently, much work has focused on exploiting these viral capsids in a *templated self-assembly* process where the geometric arrangement of the assembled capsid is used as a rigid scaffold that guides the organization of other molecules. The use of viruses to perform such templated self-assembly has been demonstrated with synthesis of structures for battery technologies [69, 70], for production of templates spheres for targeted drug delivery [71] and synthesis of pigment-protein complexes with potential to act as artificial light harvesting systems [72–74].

A popular virus scaffold that is used for templating such self-assembly is the tobacco mosaic virus (TMV), see Box 2. TMV is particularly appealing as a light harvesting structure because of the cylindrical and disk-like geometries that it self-assembles into, which closely resemble natural light harvesting complexes such as the chlorosome antenna of green sulfur bacteria (see Figure 3), and the LH2 complex of purple bacteria. To use this protein for the assembly of chromophore arrays for light harvesting, the strategy is to introduce a cysteine residue at certain positions in the capsid protein monomer, which facilitates covalent attachment of a wide variety of commercially-available chromophores. Then as the TMV capsids self-assemble the attached chromophores gather into a well-defined structure (cylinder, helix, disk) with predictable inter-chromophoric distances. Chromophores of different species can be attached to mimic donor and acceptor species and produce energetic landscapes for funneling excitation energy. Furthermore, there is a large amount of freedom in which sites of the TMV capsid monomer are modified with the cysteine residue for chromophore attachment. Using such techniques efficient and robust light harvesting behavior has already been demonstrated with broad spectrum absorption and up to 90% efficiency of energy transfer [72, 73, 75].

In Ref. [72], Miller *et al.* attached three species of chromophores to various sites along the TMV capsid protein

monomer. Then these monomers were allowed to self-assemble into disk and tubular (rod) structures. The authors estimate that such assemblies contain about 700 chromophores per 100nm of rod length, and with inter-chromophoric distances of about $20\text{\AA}$. The attached chromophores were chosen to be two donor-like pigments and one acceptor-like pigment. This allowed the investigation of energy transfer and its efficiency with different ratios of donors and acceptors. Similarly, Endo *et al.* have also incorporated two types of porphyrin based chromophores into selective sites of TMV protein monomers [73]. These monomers self-assembled into disk and rod-like structures and energy transfer in both structures was assessed. The authors estimate that the inter-chromophoric distances in their structures are about $20\text{\AA}$, and posit that the energy transfer occurs primarily through a semi-classical Förster mechanism at these length scales. This conclusion is supported by the fact that the absorption spectra of the assembled structures closely resembles monomeric absorption spectra of the chromophores (i.e., signatures of molecular aggregation, which assists coherent energy transfer, such as peak shifts and side peaks are absent). Similarly, Miller *et al.* also conclude that the energy transfer in their TMV structures is through a Förster mechanism [72]. However, it should be noted that the attachment sites of the chromophores can be changed such that their density upon self-assembly of the TMV capsids is higher than in the above two experiments, and in such structures it is expected that energy transfer will involve coherent channels. In fact, it should be noted that in earlier experiments Endo *et al.* had attached pyrene molecules to the inner-most attachment site of the TMV monomer [76]. The resulting self-assembled rod-like structures showed clear signs of strong coupling of the pyrenes, as evidenced by emission spectra consistent with excimer formation (a short-lived association of two or more molecules that is even stronger than aggregation). Therefore, we expect that by varying the attachment sites and types of chromophores attached, a TMV templated structure can interpolate between energy transfer via semi-classical mechanisms and via strongly quantum coherent mechanisms.

Box 2: The tobacco mosaic virus

The tobacco mosaic virus (TMV) is a paradigmatic example for studying self-assembly in biology. It is one of the earliest viruses studied and is structurally the best characterized. In 1955 H. Fraenkel-Conrat and R. C. Williams established that TMV self-assembles [77] by breaking apart the virus and then remixing the constituents. The mixture assembled over a period of 24 hours into intact TMV structures. Since then, much research has been conducted to understand the microscopic structure of TMV and exactly how its constituents self-assemble. TMV self-assembles into several structures depending on the conditions of solution, including a helix, 2-layer disk, or stacked disk [78]. This variety of assembled structures, and the large amount of virus that can be synthesized, are both extremely useful attributes for TMV based templated synthesis.

Structurally, the tobacco mosaic virus is composed of a tight packing of protein sub-units or monomer. These monomers self-assemble into tubular or disk like structures that encase the virus RNA [78]. Each disk has 17 protein sub-units, and tubular structures can either be composed of stacked disks or a helical arrangement of protein sub-units with $16\frac{1}{3}$ monomers per turn of the helix. The radius of the central ring in the tubular and disk structure is around $20\text{\AA}$. It is within this central pocket or elsewhere along the protein monomer that chromophores can be covalently attached using cysteine residues. The cysteine residues are not present in the natural TMV organism but can be introduced in recombinant versions.

The figure below illustrates an example of TMV-templated assembly.

Another virus that has been used to template structures with potential for light harvesting is the M13 bacteriophage. The M13 virus has ~ 2700 pVIII proteins that run the length of the virus and create a self-assembling cylindrical coat. The cylinder is roughly 880nm in length and 6.5nm in diameter. By chemically modifying the pVIII coat proteins Nam *et al.* were able to attach zinc porphyrin pigments to them [74]. By changing the ratio of zinc porphyrins to pVIII proteins they were able to modify the density of conjugated pigments on the assembled M13 virus. The average

inter-pigment separation is estimated to vary between $10 - 24\text{\AA}$. In comparison to the TMV system, the density of pigments achievable using the M13 virus is slightly smaller, and the number of pigment attachment sites that have been explored is smaller. After construction of their array of zinc porphyrins on the M13 scaffold, Nam et al. performed fluorescence, absorption and transient absorption measurements on the aggregate structure. From these measurements they conclude that there is negligible exciton delocalization in the structures due to the low density of pigments; the energy transfer was determined to take place by the Förster mechanism [74]. In addition, the authors point out that there is significant fluorescence quenching in the aggregate structures, which is conjectured to be the result of electronic coupling of multiple pigments and the creation of trap sites (although no rigorous model of this mechanism for quenching is provided) [74].

The true power of such virus-templated light harvesting structures may come from their potential to function as artificial light harvesting antennas with malleable properties. Chromophore types, densities, and orientations can in principle be tuned and adjusted. This results in an exquisite amount of control over the nanoscale structural and energetic properties of these organic assemblies. A recent theoretical analysis based on TMV-templated chromophore assemblies and employing multi-objective optimization has identified a critical trade-off that emerges between efficient energy transfer and bandwidth of photons absorbed in cylindrical chromophore assemblies [79]. The trade off is that one property cannot be maximized without sacrificing the other by modifying the arrangement and energetics of the chromophores on the cylinder. The work shows that having closely spaced chromophores and consequently strong interchromophore coupling is beneficial for negotiating this tradeoff and hence achieving high efficiency energy transfer while maintaining the spectral width of absorption in the presence of energetic and structural disorder. Therefore strong coupling and moderately delocalized excitons maybe a critical tool in maintaining good light harvesting characteristics in the presence of disorder. Understanding and developing such rational design strategies to negotiate the fundamental trade-offs involved in light harvesting is essential for developing effective and customized artificial devices that collect or sense electromagnetic radiation under diverse conditions.

It is the subject ongoing work to explore the large space of virus-templatable structures and identify optimal and robust structures that yield enhanced light harvesting or sensing performance. The key challenge in this undertaking is understanding the precise structural states of the virus-templated assemblies, including a quantitative understanding of the amount of structural disorder present and how this can be controlled. Although the assembled structures of the TMV protein and similar virus capsids are well understood, the assembled state after attachment of chromophores is less well characterized. Depending on the attachment location, linker group used to attach, and assembly conditions the chromophore array can be more or less disordered in structure. Controlling this disorder will be essential to producing replicable and reliable assemblies using this technique.

As with direct molecular aggregates, to date no virus-templated assembly of chromophores has been integrated into a device capable of utilizing the captured light energy. Schemes exist for integrating TMV-templated assemblies with electron accepting surfaces, however these have not been implemented to date and a key step that needs further investigation is the efficiency with which charge separation can be performed in such systems.

4. Engineered maquette proteins

A very different approach to protein self-assembly for generation of artificial functional biomaterials is the use of maquettes, protein scaffolds that are designed from scratch to ensure the simplest protein scaffold for a given functional task [80]. This is a synthetic biology approach that employs iterative and reversible design steps and is deliberately non-biomimetic in its means and goals. To date this emerging approach has been used to construct maquettes consisting of several (3 or 4) bundles of helices that are specifically engineered to possess specific characteristics for electron transfer [81], proton coupled electron transfer [82] or oxygen transport [83]. The explicit incorporation of quantum characteristics as a design step in such a rational synthetic approach may provide additional opportunities for generating quantum enhanced functional biomaterials in the future.

B. Radical pair materials for magnetometry

As discussed in Chapter 11, several theoretical and simulation studies have demonstrated the viability of the radical pair mechanism for detecting weak magnetic fields. Inspired by these results, Maeda *et al.* constructed a proof-of-principle experiment for demonstrating that photo-activated radical pair reactions in an artificial molecule can be sensitive to the magnitude and direction of weak magnetic fields [84]. The molecule used in their experiment was a triad composed of linked carotenoid (C), porphyrin (P), and fullerene (F) groups, see Fig. 5. Upon green-light irradiation this triad is capable to supporting a radical pair of electrons separated across almost the whole physical extent of the extended molecule. The magnetic field dependence of the recombination rate of this radical pair state

was recorded through transient absorption measurements. The authors immobilized and oriented the CPF triad by freezing it in the nematic phase of a liquid crystal. This orientation allowed the authors to demonstrate that the radical pair recombination rates were substantially altered by varying the magnitude *or* direction of magnetic fields at temperatures around 113K. This mechanism could detect magnetic field magnitude variations down to $\sim 50\mu\text{T}$, and magnetic field directional variations down to $\sim 3\text{mT}$. For comparison, the magnitude of the Earth's magnetic field is roughly $50\mu\text{T}$ (with geographic variation in the range $20\mu\text{T} - 65\mu\text{T}$). The authors comment that the molecular triad they chose is by no means an optimum magnetic field detector and therefore they expect even greater sensitivities and higher operating temperatures for optimized structures. It should be noted that there have been other experiments demonstrating the sensitivity of radical pair recombination dynamics to weak magnetic fields – e.g. Ref. [85]. However, the Maeda *et al.* experiment was the first to show that radical pair reactions are not only useful for detecting magnetic field magnitudes, but also magnetic field directionality.

FIG. 5: The triad molecular complex used by Maeda *et al.* [84] for demonstration of weak magnetic field sensing by radical pair reaction chemistry Adapted by permission from Macmillan Publishers Ltd: Nature, vol. **453**, p. 387, copyright 2008.

Although the Maeda *et al.* experiment is an encouraging start for constructing a biomimetic chemical compass based on the radical pair mechanism, many questions remain. The chief question is about exactly what type of molecular structure is best suited for hosting the photo-excited radical pair. Maeda *et al.* demonstrated that the carotenoid-porphyrin-fullerene triad was effective, but also commented that it was not optimal. Therefore what is the optimal molecular structure for building a magnetometer based on the radical pair mechanism? The specialized photoreceptor hypothesized to host the radical pair mechanism in birds is the cryptochrome flavoprotein [10] and it is possible that variants of this structure are good hosts for radical pairs. Several factors are desirable in a molecular structure for this purpose. Firstly, the photo-excited radical pair should be sufficiently separated in space as to reduce direct exchange and dipolar interactions [86, 87]. Secondly, the magnetic environments in the vicinity of the separated radicals should be as different as possible to maximize the sensitivity [85]. It has been proposed to introduce magnetic nanostructures into the design of a biomimetic chemical compass in order to maximize this asymmetry of the magnetic environments [88]. Finally, the radical pair lifetime should be long enough for the weak magnetic field to affect recombination dynamics, but not so long that spin relaxation effects dominate the dynamics [10]. The optimal lifetime will in fact depend on many of the other design details, e.g. asymmetry in magnetic environment, as well as the magnitude of the magnetic field to detect. These open questions highlight the need for a systematic study of the design rules for building an efficient radical pair based chemical compass. Such a study will greatly inform the search for molecular structures suitable for hosting the radical pairs that enable the magnetic field sensing.

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