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Photophysics of plasmonically enhanced self-assembled artificial light-harvesting nanoantennas

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The design of efficient artificial light-harvesting antennas is essential for enabling the widespread use of solar energy. Natural photosynthetic systems offer valuable inspiration, but many rely on complex pigment–protein interactions and have limited spectral coverage, which pose challenges for rational design. Chlorosome mimics, which are self-assembling pigment aggregates inspired by green photosynthetic bacteria, offer structural simplicity, flexible tunability, and strong excitonic coupling through pigment–pigment interactions. However, these pigment aggregates suffer from limited absorption in the green and near-infrared regions and, similarly to other light-harvesting systems, reduced energy transfer efficiency at high donor concentrations. One promising strategy to overcome these limitations is the integration of plasmonic nanoparticles, which enhance local electromagnetic fields, increase spectral coverage, and make new energetic pathways accessible. Although plasmonic enhancement has been widely studied in pigment–protein complexes like Photosystem I and light-harvesting complexes (LHCs), its application to pigment-pigment self-assembled systems remains largely unexplored. This perspective presents recent advances in biomimetic light-harvesting design with chlorosome mimics and explores the potential for plasmonic enhancement of photophysics in these systems. We examine the structure of chlorosomes and their artificial mimics to understand the role of pigment-pigment interactions in facilitating highly efficient energy transfer.

Designing efficient light-harvesting systems is crucial for the widespread, affordable, and safer practical use of solar radiation as a renewable energy source. The design parameters for these systems, such as near unity quantum efficiency, wide spectral coverage, cooperative energy transfer, and photoprotection, have been dictated by natural photosynthesis[1–5]. These principles have inspired biomimetic artificial light-harvesting antenna, which aim to improve energy transfer dynamics beyond those found in natural light-harvesting antennas[6–14].

One natural system studied as an inspiration for self-assembling light-harvesting systems are chlorosomes found in green photosynthetic bacteria[6,8–22]. These chlorosomes, primarily made up of thousands of bacteriochlorophyll (BChl) *c*, *d*, or *e*, are able to sustain phototropic life under extreme low-light conditions[4,16,23,24]. Chlorosomes are also unique in that their structure self-assembles through pigment-pigment interactions, as opposed to being dictated by pigment-protein interactions[4,25]. This pigment self-assembly allows for facile preparation of artificial light-harvesting antenna, and additional pigments can be easily incorporated into the self-assembling structure[26–29]. Artificial chlorosome-like structures demonstrate efficient energy transfer and strong excitonic coupling resulting in superradiance[6,15,16,30,31].

However, despite the efficient energy transfer between pigments in chlorosome-inspired artificial antennas, these systems have similar limitations as other light-harvesting complexes (LHCs). The efficiency of energy transfer decreases with an increasing concentration of pigments added to the bacteriochlorophyll structure due to limited packing space[6]. Additionally, these antennas exhibit low absorption in the green to yellow regions of the visible spectrum and in wavelengths above 900 nm, limiting their light-harvesting efficiency when compared to inorganic absorbers such as silicon[4,6,16]. Extending the absorption range and improving energy transfer efficiency would contribute towards optimizing artificial light-harvesting antennas to harness a maximal amount of sunlight.

One promising approach to addressing these limitations is the incorporation of plasmonically active nanomaterials into light-harvesting antennas[32–36]. Plasmonic behavior is a size-dependent phenomenon in which nanoparticles concentrate light to generate highly energetic charge carriers and form "hot spots" of local electromagnetic field enhancement[37].

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The nanoparticle can act as an antenna and transfer energy to molecules confined near its surface[38]. Plasmonic confinement has the potential to enhance the energy transfer efficiency between pigments by making new energetic pathways accessible and extending the range of absorption wavelengths.

Most studies on plasmonically confined photosynthetic complexes have focused on systems whose structures are governed by pigment-protein interactions, such as Photosystem I (PSI) and various purified LHCs[39–43]. In contrast, the incorporation of plasmonic nanoparticles into self-assembling systems like artificial chlorosome mimics, which rely on pigment-pigment interactions, remains largely unexplored[8].

In this perspective, we will first summarize progress in the development of bioinspired light-harvesting antennas, with a focus on design considerations in these systems. We will then examine chlorosomes and their mimics, investigating the role of pigment-pigment interactions in facilitating efficient energy transfer. Plasmonic enhancement will be introduced as an approach for addressing the shortcomings of these systems. Literature on the plasmonic enhancement of comparable light-harvesting systems will be presented to demonstrate the potential benefits of this approach. Then, we will evaluate strategies for integrating plasmonic nanoparticles into artificial chlorosome mimics. Finally, we will express our outlook on the promising future of plasmonically enhanced chlorosome mimics.

Main

Design considerations for artificial light-harvesting antennas based on natural pigments

In natural systems, the efficiency of photosynthesis strongly depends on regulation and adaptation to variable light conditions. High-light conditions necessitate dissipation of absorbed energy, since the downstream processes are what limits the rate of photosynthesis. Alternatively, low-light conditions demand that nearly all absorbed photons are utilized for photochemistry. Photosynthetic organisms in nature have met this requirement, achieving an over 90% quantum efficiency for energy transfer from light-harvesting antennas to reaction centers under optimal-light conditions[25]. For this reason, many studies devoted to increasing the efficiency of photosynthesis in vivo focus on improvements to the inefficient chemical reactions that follow, rather than light-harvesting itself[44–48].

For in vitro systems that take only the light-harvesting part of the photosynthetic apparatus and attach it to electrodes in either a solar or photochemical cell, it is possible to circumvent some of the limitations set by natural reaction centers[1]. Control over the speed of excitation conversion to separated electrons would allow high quantum efficiency to be maintained under illuminations of varying intensity. The limiting factor for such a system would then be the number of photons it can capture, although assessing the limits of artificial reaction centers comes with its own set of challenges. The obstacles faced when integrating natural light-harvesting antennas in biohybrid devices and their potential solutions have already been discussed and summarized in numerous reviews[49–52].

This perspective focuses on the optimization of one component of biohybrid devices for solar energy capture: the antenna (Fig. 1). Biomimetic antennas hold great promise due to the near-unity quantum efficiencies found in nature, but there is room for improvement in terms of the spectral coverage of these systems. For example, natural light-harvesting antennas, with the exception of phycobilisomes, generally do not absorb much green light. While researchers provide proposed explanations for why most photosynthetic organisms do not absorb this abundant region of light[53,54], in biohybrid devices, any part of the solar spectrum that is ignored yields lower overall efficiency. Another range of underutilized light is the red to infrared region, as most natural light-harvesting antennas do not use these wavelengths for photosynthesis.

Concerted efforts to extend the absorption range of light-harvesting antennas have focused on designing proteins to tune spectral gaps of pigments or bind modified absorbers[55,56]. Some approaches to constructing artificial light-harvesting systems, such as those based on dendrimers of dyes, organic nanocrystals, or non-covalent assemblies, have been also been studied[11,12,57–59]. Others have focused on incorporating natural pigments with unique optical properties, such as chlorophyll (Chl) *f*. Prior to the discovery of Chl *f* in 2010[60], it was believed that only anoxygenic photosynthesis could utilize wavelengths of light beyond 680 nm, as oxygenic photosynthesis was considered to be limited by the high redox potential necessary to split water. Far-red-light-adapted organisms with antennas containing Chl *f* suggested otherwise, demonstrating that longer wavelengths of light could be utilized in oxygenic photosynthesis[60–62]. Incorporating Chl *f* in modified photosynthetic antennas broadened their absorption range, demonstrating potential for applications in photoelectrochemical cells for hydrogen or fuel production from photocatalytic water splitting[63]. However, these systems showed poor overall stability and efficiency, limiting their practical use[64].

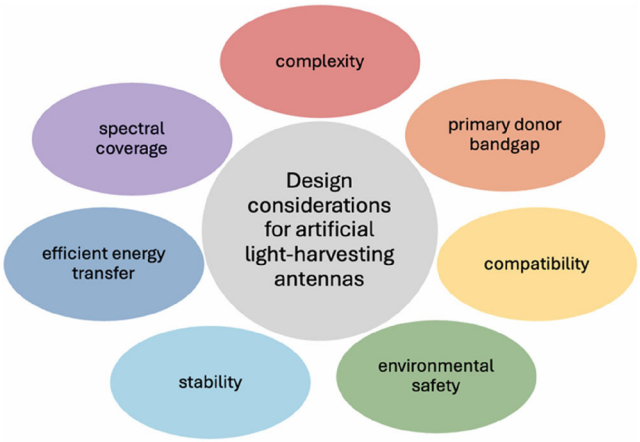

Fig. 1 | An overview of different aspects to consider for the design of an efficient light-harvesting antenna. The antenna must absorb as much of the solar spectrum as possible. A simple preparation procedure is desirable to lower production costs. The internal quantum efficiency of multicomponent systems hinges on efficient energy transfer between individual components. The bandgap of the lowest-energy component determines the energy efficiency. Long-term stability under working conditions is necessary. The antenna must be compatible with other parts of the device incorporating it. Preferably, nontoxic components or processes are used for preparation.

To improve stability and ease of practical application, other efforts to modify light-harvesting antennas have explored self-assembling systems. In 2022, Hancock et al.[65] studied self-assembled liposomes with a combination of natural complexes and synthetic dyes. Energy transfer was demonstrated between components without covalent binding or other modifications of said natural complexes. Lipophilic dyes and lipid-bound hydrophilic dyes were used to sensitize LHCII from plants and LH2 from bacteria, and an 80% boost in fluorescence from the acceptor was recorded. In 2025, they followed up with increased generation of photocurrent directly from sensitized LHCII in an identical system[66]. This shows potential for utilization of such artificial self-assembling membranes in light-harvesting.

Other studies have focused on the design of self-assembled light-harvesting antennas themselves. Chlorosomes, antennas of green bacteria that are mostly composed of pigments, are an inspiration for a whole other class of self-assembled absorbers (Fig. 2a). Bacteriochlorophylls isolated from these antennas have shown the ability to self-assemble in vitro into units that are functionally very similar to chlorosomes themselves. Modifications of these artificially self-assembled antennas have been studied with the intent to develop an antenna with an extended absorption spectrum[6,19,28,29,67–69].

Chemically modified bacteriochlorophylls have been used to prepare artificial chlorosome-like antennas with optimized spectral properties. Selective substitution of functional groups of the chlorin ring was shown to tune absorption properties of individual pigments[67,70], partially covering the green gap or red-shifting absorption[71]. In other studies, co-assemblies of natural bacteriochlorophylls with other pigments have been

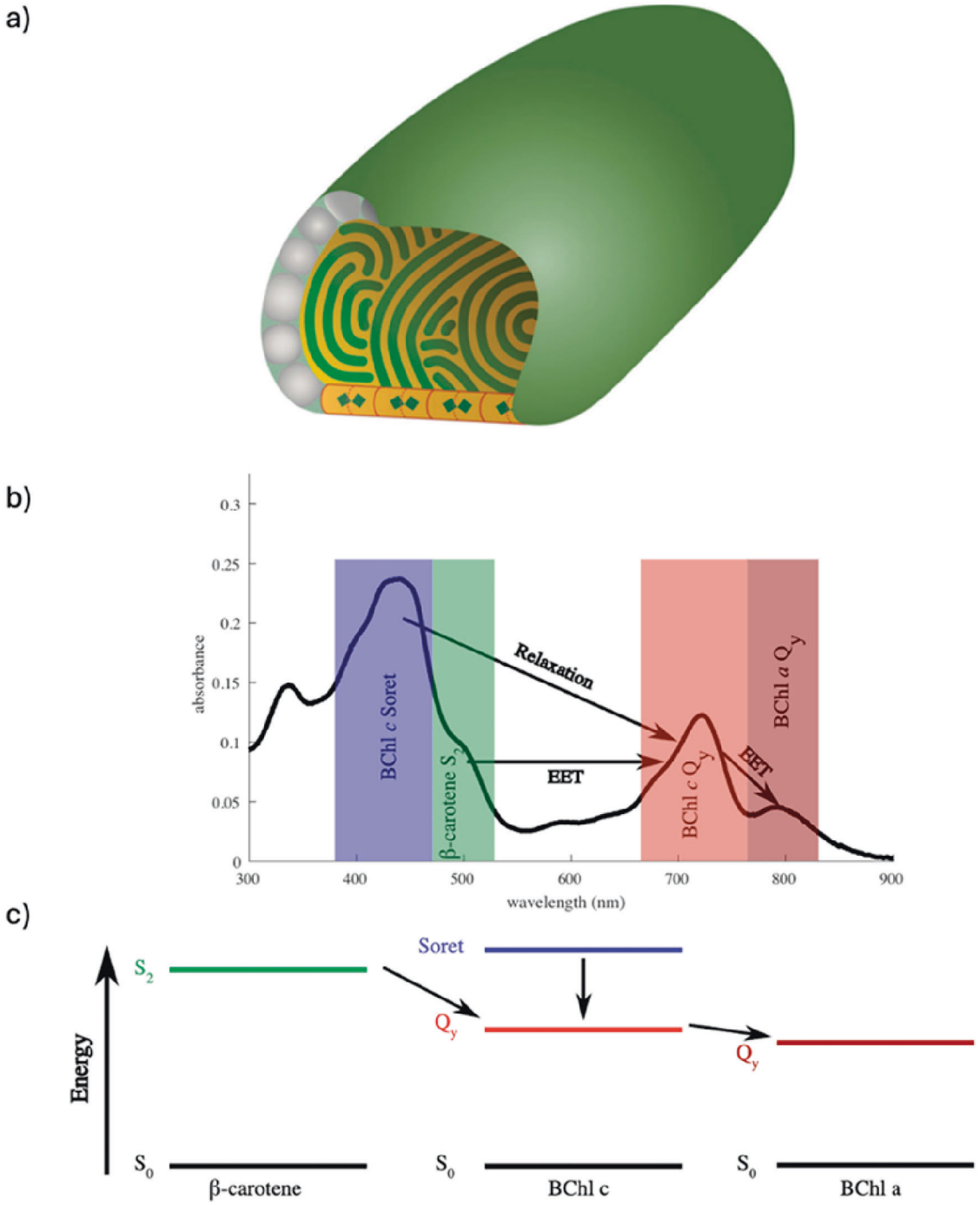

Fig. 2 | Photophysics and structural considerations of chlorosomes. a The diagram illustrates the shape and interior structure of a typical chlorosome. The lamellar layers (shown in green) consist of aggregates of bacteriochlorophyll (BChl). These layers are held together by hydrophobic interactions between the interdigitated esterifying alcohols of the BChls, which create a hydrophobic space (depicted in orange) between the chlorin layers. This space is also occupied by carotenoids and quinones. At the base of the chlorosome, the baseplate is represented as being composed of CsmA protein dimers, each containing one BChl a molecule (represented as a blue-green rectangle). The orange background of the baseplate indicates the presence of carotenoids within it. The envelope is primarily made up of proteins (illustrated as gray particles), while lipids fill the space between the proteins (shown in cyan). Reprinted from reference 17, © 2014, with permission from Springer Nature. **b** An absorbance spectrum of artificial chlorosome mimics, which are pigment aggregates made up of BChl a, BChl c, and β-carotene. Arrows indicate the flow of electronic energy transfer and relaxation within the aggregates. **c** A conceptual energy level diagram illustrating the flow of energy transfer in artificial chlorosome mimic pigment aggregates.

demonstrated[19,26–29,68,69]. Recently, efficiency of energy transfer between components in a three-pigment self-assembled antenna was determined (Fig. 2b, c)[6].

While self-assembling multi-component light-harvesting antennas provide, in theory, a relatively simple solution to the search for a panchromatic photosynthetic absorber, it is important to consider the efficiency of energy transfer between individual components. Although many dyes can transfer excitation energy to photosynthetic complexes, they do not all exhibit optimal efficiency. In the previously mentioned case of liposomes[65], the efficiency of energy transfer to LHCII ranged between 25

and 97% depending on the dye and concentration, and the efficiency of energy transfer to LH2 ranged between 53 and 91%. The recorded 97% efficiency corresponded to energy transfer from Texas Red to LHCII, but the efficiency was significantly lowered with increasing the donor concentration.

Similar conclusions were found for chlorosome mimics. One study loaded a bacteriochlorophyll structure with carotenoids, which transferred almost 90% of excitations at low carotenoid content, but efficiency dropped with higher donor concentration[6]. Thus, for practical applications, the efficiency of energy transfer, light-harvesting, or both must be improved in order for multi-component systems to be used as absorbers.

Structure-function relationship within natural and artificial bacteriochlorophyll aggregates

Chlorosomes and their artificial mimics have great potential in solar energy harnessing due to their high number of pigments, efficient energy transfer, and simple preparation procedures. Although the pigments in these systems can harvest light fairly well on their own, it is only upon aggregation that exciton delocalization occurs[4,16,17], which contributes to a high excitation energy transfer efficiency despite the large size of these systems[72,73]. Therefore, a robust understanding of the role of pigment-pigment interactions in these systems is needed to guide rational design for the incorporation of plasmonic nanoparticles into chlorosomes.

The large size of the chlorosome and the high degree of heterogeneity and disorder[4,16,17] make pigment organization in each chlorosome unique, preventing structure determination by X-ray crystallography or single particle averaging. X-ray scattering and cryo-EM studies have revealed repeating layers of pigments exhibiting lamellar organization[74]. This layered arrangement has since been confirmed by many other studies[75–81].

The formation of layers is enabled by the structure of chlorosomal BChls[76]. Individual BChls are bound together by π-π interactions, with bonds between the central metal ion and the alcohol and keto groups leading to the formation of 2D layers[82]. These layers are held together by van der Waals interactions between the esterifying alcohols of BChls. The same bonding structure is found within artificial chlorosome mimics, suggesting that the layered nature of aggregates is embedded within the structure of the BChl molecules themselves[83]. The aggregates adopt various structures, from the disordered curved lamellae found in most of the native chlorosomes to the cylinders found in specific mutants with a simplified composition[75,81,84–87].

The strong interactions between pigments in both natural and artificial chlorosomes yield several distinct effects when compared to individual pigments. Excitonic interactions give rise to red-shifted and broadened absorption bands when compared to those of monomeric pigments. Strong coupling between BChls results in exciton delocalization, which can extend over many pigments[15,16,88,89]. In fact, the excitation interactions between pigments are so strong that they maintain some extent of delocalization even after exciton relaxation, causing aggregates to exhibit superradiance[15]. These strong pigment-pigment interactions also give rise to structural domains separated by inhomogeneities or structural variations where pigments interact more strongly[90,91], which may allow for Förster hopping between these domains and increase the efficiency of energy transfer by limiting the number of hopping steps[72,73,91–93].

Towards the development of artificial aggregates, chlorosomal bacteriochlorophylls have been found to aggregate both in non-polar solvents and in aqueous environments. Aggregation in aqueous solvents is driven by interaction between the non-polar esterifying alcohols, and addition of a suitable non-polar molecule is required to induce the aggregation[19,68,69]. Aggregation in non-polar solvents is driven by interactions between the polar chlorin rings[94]. This ability to self-assemble under various conditions adds versatility to preparing co-assemblies of plasmonic nanoparticles with chlorosome mimics. The hydrogen and coordination bonds within bacteriochlorophyll aggregates indicate that attaching them to functionalized nanoparticles is possible, which has been confirmed experimentally by growing BChl aggregates on gold surfaces functionalized with hydroxyl groups[8].

Their self-assembly, the ability to incorporate other pigments into their structure, and the potential for their attachment to functionalized surfaces of plasmonic nanoparticles make chlorosome mimics promising candidates for plasmonically enhanced light-harvesting antennas. The gaps in chlorosomes' absorption spectra between 500–700 nm and above 900 nm are one downside of these systems that the incorporation of plasmonic nanoparticles would improve. This, along with other ways that plasmonic confinement can enhance the photophysics of chlorosomes, will be discussed in the following sections.

Plasmonic nanoantennas as "super" sensitizers to enhance light-harvesting antennas

Recently, plasmonic nanoantennas have been applied to extend the absorption range and enhance the photophysics of light-harvesting systems. Plasmonic nanoparticles offer the advantages of extended spectral coverage[34,95], enhanced light-harvesting abilities in nearby molecules[96], and easily tunable optical properties[97–99]. In this section, we will discuss how plasmonic nanoparticles can act as "super" sensitizers and enhance the photophysics of light-harvesting antennas. For literature focused on comprehensive analyses of related topics, readers are referred to reviews on plasmonic behavior[37], plasmonic photochemistry[100–102], and surface-enhanced Raman spectroscopy (SERS)[103].

A surface plasmon is defined as a collective oscillation of delocalized electrons that is induced by irradiation with light[37,104]. There are two types of surface plasmons: the surface plasmon polariton (SPP) (Fig. 3a) and the localized surface plasmon resonance (LSPR) (Fig. 3b)[37]. SPPs are traveling electromagnetic waves that propagate across a thin metal surface, while LSPRs are localized to a nanoparticle.

For plasmonic applications in biomimetic light-harvesting systems, we have chosen to focus on the LSPR. One reason it is desirable to work with the LSPR is because plasmonic nanoparticles offer the advantage of great flexibility. The LSPR frequency can easily be tuned by adjusting the nanoparticle shape, size, or material, which allows for precise control when integrating into complex light-harvesting systems (Fig. 3c, d)[105–107]. Another reason for working with the LSPR is that LSPR excitation and decay present several opportunities for charge and energy transfer that can enhance the photophysics of nearby molecules[37,38]. During LSPR decay, highly energetic charge carriers are generated that can transfer to nearby molecules or recombine, resulting in thermal dissipation (Fig. 3e)[37]. LSPR excitation concentrates light to "hot spots" of localized electromagnetic field enhancement, the strength of which can be described by the electromagnetic enhancement factor $L(\nu)$ relating the amplitude of the local field $|E_{Loc}|$ with that of the incident electromagnetic field $|E_0|$(Eq. (1))[108–110]

$$L(\nu) = \frac{|E_{Loc}(\nu)|}{|E_0|} \tag{1}$$

This enhancement comes from two main contributions: a wavelength-dependent component from the resonant excitation of localized surface plasmons in metallic nanostructures ($L_{SP}(\nu)$) and a geometric component called the "lightning rod effect" (L_{LR}) (Eq. (2))[108,110,111]

$$L(\nu) = L_{SP}(\nu)L_{LR} \tag{2}$$

This "lightning rod effect" refers to the crowding of electric field lines at the junctions between nanoparticles and sharp geometric features, which explains why those regions experience the most intense electromagnetic enhancement (Fig. 3f)[111]. The $L_{SP}(\nu)$ is directly proportional to the g factor derived through Mie Theory (Eq. (3)) that relates the dielectric function of the plasmonic nanoparticle ($\varepsilon(\omega)$) and the dielectric constant of the surrounding medium (ε_m)[37,104,108,112]. Maximal electromagnetic field enhancement is achieved when the g factor is maximized by meeting the Frölich

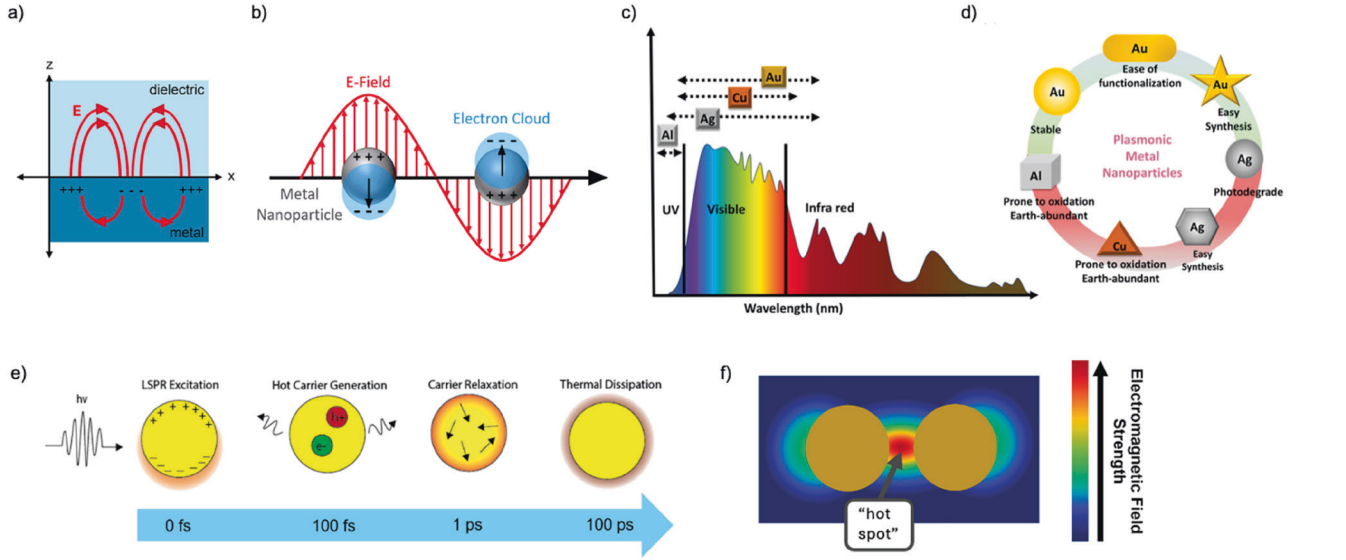

Fig. 3 | Surface plasmon resonances across varied spectral regimes on rapid timescales. Schematics showing the transformative potential of plasmonic materials, where in **a**, we see a compelling illustration of the surface plasmon polariton, while part **b** showcases localized surface plasmon resonance, both of which are foundational concepts in this field. Part **c** offers a critical summary of the key absorption spectral ranges of various plasmonic metals, highlighting their potential in harnessing the expansive solar spectrum through diverse shapes and sizes of metal nanoparticles. Reprinted with permission from ref. 117, Copyright © 2024 by the American Chemical Society. In part **d**, a schematic comparison of the optical and physical properties of noble and non-precious plasmonic metal nanoparticles reveals significant differences that drive innovation in material design. Reprinted with permission from ref. 117, Copyright © 2024 by the American Chemical Society. Part **e** presents a dynamic schematic that captures the timescale of plasmon excitation and its time-resolved progression, providing a clearer understanding of these rapid processes. This illustration is reprinted with permission from ref. 37, Copyright © 2024 by AIP Publishing. Finally, part **f** introduces the concept of "hot spots," showcasing the remarkable electromagnetic field enhancement occurring at the junction between two plasmonic nanoparticles. All mechanisms underscore the intricate interactions at play in plasmonics for light-harvesting.

condition for plasmonic behavior (Eq. (4))[112]

$$g = \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \tag{3}$$

$$\varepsilon(\omega) = -2\varepsilon_m \tag{4}$$

"Hot spots" of this electromagnetic field enhancement exhibit changes in polarizability and shifts in the adsorbate molecular orbital overlap with the density of states in the plasmonic metal[37,108,112]. This is notable because it can modify fluorescence[109,113–115], absorption[116], and scattering processes[109,110] in plasmonically confined molecules.

The effects of plasmons on nearby molecules, from both electromagnetic hot spots and highly energetic charge carriers, enable plasmonic nanoantennas to be thought of as "super" sensitizers. Not only do plasmonic nanoparticles act as conventional photosensitizers by extending the absorption range of a system, but they also make new energetic pathways accessible for nearby, plasmonically confined, molecules[37,38,117].

Research into this aspect of plasmonics is relatively young. Although plasmonic behavior has been studied since the 1970s[118–121], initial research on plasmonics was limited to applications in spectroscopy and imaging. This changed in 2010, with the first report of a plasmon-driven chemical transformation[122]. In this work, Huang et al. observed the oxidation of para-aminothiophenol to form 4,4′-dimercaptoazobenzene during SERS measurements on a silver plasmonic substrate[122]. This discovery ushered in a new era for the field of plasmonics, extending research into applications in surface catalysis and light-harvesting systems.

Effects of plasmonic enhancement in photosynthetic complexes

Plasmonic confinement of natural photosynthetic complexes has been shown to offer several benefits, such as extended absorption ranges[123], enhanced energy transfer and absorption[114,124], and increased photostability[114,125]. The plasmonic nanoparticles used in these systems are most commonly either silver or gold, since silver offers strong electromagnetic field enhancement and gold offers great stability[37]. Natural photosynthetic complexes that have been studied under plasmonic confinement include Photosystem I (PSI)[126], Photosystem II (PSII)[127], light-harvesting complex II (LHCII)[128], light-harvesting complex 1 (LH1)[123], light-harvesting complex 2 (LH2)[114], and peridinin−chlorophyll−protein (PCP)[129]. Plasmonic confinement of chlorosomes or their artificial mimics has not yet been studied, but examining the impacts of plasmonic enhancement on other natural photosynthetic systems enables the development of a hypothesis for how plasmonic confinement could benefit chlorosomes and their artificial mimics.

Plasmonic nanoparticles can extend the absorption range of light-harvesting systems through rational design of the optical overlap between the nanoparticle and the photosynthetic complex. For example, the limited absorption capability of both LH1 and LH2 between ~600 and 800 nm can be compensated for by incorporating gold nanoparticles that have an LSPR frequency in this region and strongly absorb this light (Fig. 4)[123]. Chlorosomes and their mimics similarly have limited absorption in the 500–700 nm region, so the incorporation of gold nanoparticles could be used to achieve a more robust absorption spectrum in plasmon-chlorosome hybrid systems.

To examine enhanced energy transfer and absorption, many studies on plasmonically confined natural photosynthetic complexes focus on fluorescence spectroscopy and maximizing fluorescence signal intensity[32,34,35,100,126]. Plasmonic confinement of fluorophores can result in either fluorescence quenching or enhancement, depending on factors such as optical overlap and the distance between the nanoparticle and fluorophore molecule (Fig. 5)[130]. Fluorescence enhancement is understood to occur by enhancing the molecule's absorbance or by increasing the radiative rate of the plasmonically confined species[114]. Absorption enhancement depends on the degree of overlap between the LSPR scattering spectrum and the chromophore's absorption spectrum, while the increased radiative rate depends on strong plasmonic enhancement

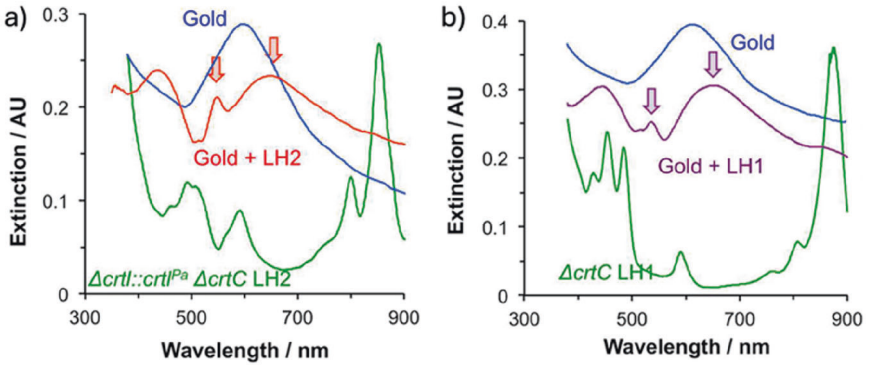

Fig. 4 | Optical signatures for light-harvesting biomimetic systems. Extinction spectra for gold nanostructured periodic arrays before (blue) and after (red) attachment of **a** the Δcrtl::crtlPa ΔcrtC mutant of LH2 and **b** the Δ*crtC* mutant of LH1. Arrows indicate new peaks formed from the energetic splitting of the LSPR. The absorption spectra of solvated proteins are shown in green. Reprinted with permission from ref. 123, Copyright © 2024 American Chemical Society.

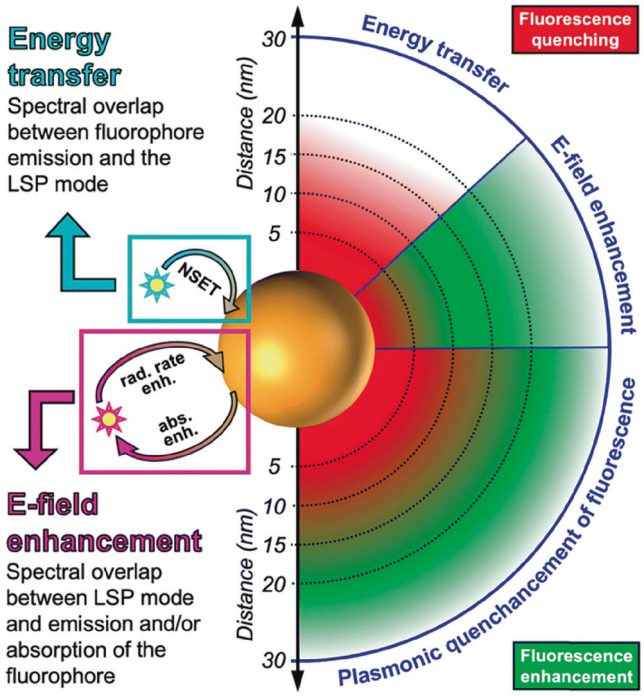

Fig. 5 | Schematic showing how different factors contribute to plasmonic fluorescence enhancement and quenching. Fluorescence quenching is experienced by fluorophores near the nanoparticle surface due to strong energy losses involving the scattering of electrons in the metal. The enhancement of the electric field (E-field) through localized surface plasmons (LSPs) on plasmonic nanoparticles leads to increased absorption and/or radiative rate for adsorbed fluorophores, extending up to several tens of nanometers (approximately 30 nm, as shown here). Nanosurface energy transfer (NSET) occurs between the transition dipole moment of the fluorophore emission and the LSPs on the nanoparticle, resulting in a distance-dependent enhancement or quenching of the signal. Typically, both NSET and E-field enhancement happen concurrently, resulting in a combination of quenching and enhancement, referred to as "quenchancement." Reprinted from ref. 130 with permission from The Royal Society of Chemistry.

of the local electromagnetic field[130]. Increased fluorescence signals can also signify increased energy transfer between chromophores in multicomponent systems, which is desirable for optimal light-harvesting[124]. It can be challenging to deconvolute the factors contributing to fluorescence enhancement and quenching, but studying changes in fluorescence does have great potential to reveal information about the photophysics of plasmonically confined light-harvesting systems.

Plasmonic confinement has been shown to enhance the absorption of natural photosynthetic complexes, resulting in considerable fluorescence enhancement. Czechowski et al. reported a fluorescence enhancement factor of ~200 for PSI when placed under the plasmonic confinement of silver nanoparticles[124]. Since fluorescence lifetimes were not changed by plasmonic confinement, the signal enhancement was attributed to plasmonic activation of new excitation and emission channels in PSI[124]. For LH2, an over 500-fold plasmonic fluorescence enhancement has been observed at the single-molecule level, which was partially attributed to excitation enhancement from the LSPR[114]. Since enhanced photon absorption and newly accessible energetic pathways are common in other plasmonically confined light-harvesting systems, it is reasonable to hypothesize that this may occur in plasmonically confined chlorosomes as well.

Plasmonic confinement can also increase the photostability of light-harvesting systems. The plasmonically enhanced local electromagnetic field can cause radiative rate enhancement, which improves photostability by minimizing the amount of time that the plasmonically confined species exist in an excited state, allowing for an increased number of photons to be emitted before any photodamage occurs[114]. Additionally, interaction with the plasmonic nanoparticle can protect chromophores from degradation, which is shown in the example of gold nanoparticles preventing the degradation of Chl *a* from reactive oxygen species by binding with the pigments at nitrogen sites[125]. For chlorosomes, some photoprotection is already provided by the carotenoids and quinones in the structure and the excitonic interactions between aggregated pigments, but further stability provided by plasmonic nanoparticles would be beneficial.

Design strategies for the integration of plasmonic nanoparticles into artificial chlorosome mimics

Despite the promising effects observed in plasmonically enhanced natural photosynthetic pigment-protein complexes, there is a lack of research on plasmonic confinement of chlorosome structures or their artificial mimics. Given that plasmonic enhancement is highly dependent on the location of confined molecules relative to plasmonic nanoparticles and their "hot spots," it is important to discuss strategies for integrating nanoparticles into chlorosome-like structures to obtain maximal plasmonic enhancement.

The first design consideration for these systems is the selection of plasmonic nanoparticles. Plasmonic nanoparticles can vary in their size, shape, and composition, which all influence the LSPR frequency and the electromagnetic field enhancement[105–107]. Although recent reviews have focused on silver plasmonic systems due to their strong plasmonic activity[131], we advocate for the use of gold nanoparticles due to their superior stability that simplifies sample handling and spectroscopic characterization. Additionally, gold nanoparticles offer a high degree of functional versatility. They can be readily modified with various ligands such as citrate[132], cetyltrimethylammonium bromide[133], or thiol-containing compounds[8], which enable diverse attachment strategies to tune interactions with chlorosome mimics. Gold nanoparticles have been synthesized in a variety of morphologies, including spheres[134,135], rods[133,136], cubes[98,137,138], and stars[139,140], which offers additional flexibility in design.

Particle shape is an important factor affecting plasmon-molecule interactions, due to the previously discussed geometric dependence of

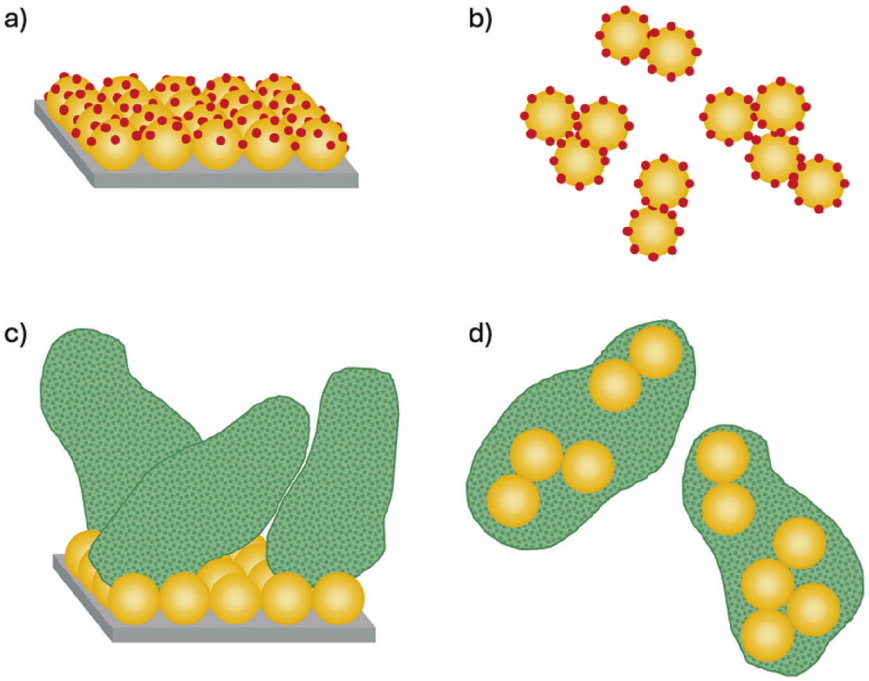

Fig. 6 | Design concepts for pigment-nanoparticle interactions. Schematic showing plasmonic confinement of small molecules via **a** a solid-phase plasmonic substrate and **b** solution-phase nanoparticle aggregation. Since artificial chlorosome mimics are quite large compared to the size of plasmonic nanoparticles, the number of pigments placed under plasmonic confinement is limited for **c** solid-phase plasmonic substrate compared to **d** when nanoparticles are embedded within the chlorosome mimics via simultaneous pigment and nanoparticle aggregation.

electromagnetic field enhancement[108]. Maximizing the number of "hot spots" accessible to chlorosomal pigments requires a nanoparticle shape with several sharp geometric features, since these yield the highest electromagnetic field enhancement. Shapes such as nanostars or nanorods are promising, not only because of the number of hot spots per particle, but also because their anisotropy supports multiple LSPR frequencies, enabling use of a wider range of wavelengths.

Size is another important parameter, as larger particles exhibit red-shifted LSPR frequencies and smaller particles exhibit blue-shifted LSPR frequencies[105]. Tuning the nanoparticle size is a simple way to control the optical overlap between the nanoparticle's LSPR and the absorption of the chlorosomal pigments. Gaps in the absorption spectrum of artificial chlorosome mimics, particularly in the 500–700 nm and >900 nm regions, can be compensated for with nanoparticles that absorb those wavelengths. Alternatively, nanoparticles can be designed to have an LSPR that matches specific pigment absorption features, such as that of BChl *c*, to enhance energy transfer processes toward BChl *a*. Together, these design options offer multiple viable approaches for optimizing plasmon-molecule interactions, enabling efficient broadband light-harvesting.

Beyond nanoparticle selection, a crucial design consideration is the method used to place chlorosomal pigments under plasmonic confinement. There are two main strategies for this: immobilization on solid-phase plasmonic substrates (Fig. 6a)[141,142] or solution-phase nanoparticle aggregation (Fig. 6b)[132]. In the first approach, solid-phase plasmonic substrates, such as nanoarrays of functionalized nanoparticles, would be fabricated via lithography, and previously prepared chlorosome mimics would be deposited on their surfaces[141,142]. However, since chlorosome mimics are quite large, attachment in this manner would place only a small fraction of the pigments within the "hot spot" regions of the plasmonic substrate, leaving the majority of pigments unaffected (Fig. 6c).

To maximize the amount of chlorosomal pigments placed under plasmonic confinement, incorporating nanoparticles within the structure is a promising approach (Fig. 6d). This could be achieved using the solution-phase nanoparticle aggregation method. In this approach, colloidal nanoparticles are dispersed in solution, and pigment molecules are introduced to destabilize the dispersion, triggering nanoparticle aggregation[132]. The nanoparticles form dimers, trimers, and larger oligomers with "hot spots" at each nanoparticle junction. If needed, excessive aggregation and precipitation can be prevented by adding a polymer that will form a shell around the oligomers, stopping the aggregation process[132]. If chlorosomal pigments were added to a colloidal nanoparticle dispersion, the simultaneous formation of pigment aggregates and nanoparticle aggregates could occur. Electrostatic attractions or hydrogen bonding between the pigments and the functionalized nanoparticle surface could cause the nanoparticles to form aggregates within the chlorosome structure. Embedding the plasmonic aggregates within the larger chlorosome structure would allow for plasmonic confinement of a larger portion of the chlorosomal pigments, amplifying plasmonic enhancement effects. The structural disruption caused by the presence of the nanoparticles themselves could also alter the excited-state dynamics, independent of plasmonic enhancement effects. Such a phenomenon was recently observed[6] when additional pigments were added into the structure of bacteriochlorophyll aggregates and an increase in total fluorescence was observed. However, the effects of plasmonic nanoparticles in these circumstances are still largely unexplored.

Outlook

In conclusion, this perspective emphasizes the untapped potential of plasmonic enhancement in self-assembling artificial light-harvesting systems. We have summarized the design considerations that guided previous development of nature-inspired light-harvesting systems, highlighting why chlorosomes are particularly promising as a source of inspiration for artificial light-harvesting systems. We examined the effects of plasmonic confinement on light-harvesting systems, considering the potential benefits this could have on chlorosomes and their mimics. We assert that the plasmonic confinement of artificial chlorosomes is worth investigating. Self-assembling chlorosome mimics offer the advantages of simple fabrication and efficient energy transfer, and high photostability. We believe that there is potential for exciting future work in the design and optimization of plasmon-chlorosome systems, as the synergy between the light-absorbing abilities of plasmonic nanoparticles and the enhanced photophysics and photostability of plasmonically confined molecules holds promise for the development of light-harvesting systems with unprecedented light-harvesting efficiency.

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Author contributions

E.D.: conceptualized the perspective; prepared figures; wrote introduction, plasmonics, and outlook sections; and edited and reviewed manuscript. T.M.: prepared figures; wrote section on design considerations for artificial light-harvesting antennas based on natural pigments; and edited and reviewed manuscript. E.S.: contributed to plasmonics section, and edited and reviewed the manuscript. J.P.: edited and reviewed manuscript. E.A.S.-K.: conceptualized the perspective; supervision; edited and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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