Plasmon-Controlled Light-Harvesting: Design Rules for Biohybrid Devices via Multiscale Modeling

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Supporting Information

ABSTRACT: Photosynthesis is triggered by the absorption of light by light-harvesting (LH) pigment–protein complexes followed by excitation energy transfer to the reaction center(s). A promising strategy to achieve control on and to improve light harvesting is to complement the LH complexes with plasmonic particles. Here a recently developed QM/MM/continuum approach is used to investigate the LH process of the peridinin-chlorophyll-protein (PCP) complex on a silver island film. The simulations not only reproduce and interpret the experiments but they also suggest general rules to design novel biohybrid devices; hot-spot configurations in which the LH complex is sandwiched between couples of metal aggregates are found to produce the largest amplifications. Indications about the best distances and orientations are also reported together with illumination and emission geometries of the PCP–NP system necessary to achieve the maximum enhancement.

KEYWORDS: Plasmon enhancement, pigment–protein complexes, fluorescence, light-harvesting, multiscale QM/classical models

The most abundant renewable energy source available in our planet is solar radiation; its capture for energy production and storage, efficiently converting it into chemical or electrical energy, is one of the grand challenges of the next decades.1−3 Natural photosynthetic systems do that to live and grow through the complex ensemble of photosynthetic processes.4 Photosynthesis is triggered by the absorption of light by pigment–protein complexes (light-harvesting, LH, complexes) followed by funneling of the resulting electronic excitation energy to the photosynthetic reaction center(s). These antenna systems consist of either highly ordered or apparently random arrangements of pigments bound to a protein scaffold5 that collect photons and trap solar energy with high efficiency. A clever idea would therefore be that of working out how Nature has mastered the efficient capture of the Sun and use this knowledge to design nanodevices that can direct, sort, and respond in sophisticated ways to excitation energy. As a matter of fact, Nature uses the environment as a controller and a regulator; for example, the protein plays a fundamental role in optimizing the light-harvesting by organizing the pigments and tuning their “site” energies. Moreover, recent discoveries seem to show that quantum coherence is involved in the transport of electronic excitation,6−9 and that the protein also plays a role in keeping this coherence through a combination of slow and spatially correlated fluctuations.10,11

A promising strategy to achieve control on and to improve light harvesting is to complement the natural environment of LH complexes with plasmonic particles. Strong enhancement of electromagnetic fields generated through surface plasmon resonances (SPR) in metal films and nanoparticles (NP) has recently stimulated a large interest due to their enormous versatility in affecting absorption, fluorescence, and excitation energy transfer (EET) of nearby located molecular systems.12−19 In parallel, photosynthetic pigment–protein complexes have been also combined with metal NPs in order to explore bioinspired strategies for the construction of efficient hybrid LH devices.20−22 In all the considered systems, the net change of the fluorescence is the result of a delicate balance among competitive effects. In fact, metal NPs generally enhance the radiative decay rates of acceptors as well as the initial process of electronic absorption of the donors but they can also act as competitive energy acceptors as well as they can directly affect the electronic coupling determining the EET. Moreover, all these processes do not only depend on the characteristics of the NP (its nature, shape, and dimension) but also on its position and orientation with respect to the pigments as well as on the solvent. It is therefore of fundamental importance to develop multiscale models that can describe the actors into play (the pigments, the protein—solvent environment, and the NPs) in a mutually polarized way and at the same time can artificially decouple the interactions so to understand their specific contribution to the full process. Here we report the first
application of an accurate multiscale quantum-mechanical (QM) approach to describe the effects of metal NPs on the capture of photons and the transfer of excitation energy in a LH complex. In particular, our novel approach is based on a three-layers formulation using a QM description for the pigments, a polarizable MM force field for the protein, and a continuum description for the metal NPs and the solvent. In all cases, each different component of the system mutually interacts with the others and the QM description of the electronic processes (absorption, energy transfer, and emission) includes the effects of the classical parts in a self-consistent way. The multiscale approach here is applied to the simulation of the experimentally observed enhancement of the fluorescence of chlorophylls in the PCP LH complex when deposited on a silver island film, allowing a dissection of the overall enhancement in elementary contributions. Following the results obtained for this investigation, rules for designing an optimal biohybrid device to obtain controllable light-harvesting using natural systems and NPs are finally proposed.

PCP, a water-soluble peripheral LH antenna from dinoflagellate Amphidinium carterae, presents a trimeric quaternary structure with each monomer consisting of two domains...
The domains are related by a two-fold pseudosymmetry axis and each encloses a central chlorophyll a (CHL) surrounded by four peridinins (PID). In each monomeric form, the two CHL and the eight PID pigments are closely packed (see Figure 1b). PCP utilizes the PID as its primary pigment, which is responsible for the dominant absorption band in the blue-green spectral region (350 to 550 nm), whereas the fluorescence of PCP originates from the Q_y transition of CHL and it is located at 673 nm (see Figure 1d). Mackovski et al. have shown that plasmonic excitation of randomly deposited PCP complexes on a silver island film (SIF) induces dramatic fluorescence enhancement in individual pigment–protein complexes with no remarkable influence on the emission energy. The fluorescence enhancement was observed both when the CHL molecules are directly excited (at 632 nm, corresponding to the blue wing of the Q_y band), and when the PID molecules are excited (at 532 nm). The two excitations initiate two completely different mechanisms. At 632 nm, only the CHL molecules are excited and the observed enhancement (8.5 in average) is related to the direct interaction of the chlorophylls and the MNP(s). On the other hand, the excitation at 532 nm corresponds to the PID absorption and the observed enhanced fluorescence (by an average factor of 6 and a maximum of 18)
is due to the plasmonic interaction with both CHL and PID molecules with the CHL excited states populated via a subsequent energy transfer. The measured average enhancements result from the broad distribution of fluorescence enhancement factors for individual PCP complexes due to the size variation of Ag nanoparticles in the SIF layer. Atomic force microscopy image of the SIF surface shows in fact a heterogeneous metal system made of Ag islands with diameters ranging from 70 to 140 nm, and heights between 30 and 40 nm. In addition, the interaction between the metal surface and the pigments depends on the relative distance and on orientation. To account for both heterogeneity and geometrical arrangements, we have considered different PCP–NPs setups as well as we have analyzed the distance and the orientation dependence. In regard to the metal system heterogeneity, we have considered silver spherical particles of radius 30 nm and aggregates made of two or three fused spherical particles having a major axis of 90 and 120 nm, respectively (see Figure 1b). For sake of convenience, here and in the following we will refer to the above aggregates with the labels of single sphere (S), double sphere (D), or triple sphere (T) particles. In addition, we have also considered the possibility of two particles and/or aggregates close enough to present plasmon couplings that can modify their optical properties (see Figure 1e).

All possible PCP–metal arrangements are here described using a multiscale approach consisting of three coupled layers. The chlorophyll and peridinin pigments involved in the electronic processes (absorption, EET, and fluorescence) are treated quantum-mechanically. The protein matrix and the cofactors present in the PCP are treated classically in terms of apparent charges placed on its surface. Two different MMplool environments have been used, a small one (called minimal environment) that includes the full dimeric complex (8 peridinins, 2 chlorophylls, and the 2 lipids, digalactosyl diacyl glycerol, which are an integral part of the complex in the crystal structure) and a large one containing the full protein matrix. All the details of the computational strategy used are reported in the Supporting Information.

The metal-induced fluorescence enhancement can be obtained for a donor–metal–acceptor system in stationary conditions under the assumptions of selective irradiation of the donor and in the absence of the back-energy transfer from the acceptor to the donor, by defining the kinetic equations for a statistical ensemble of molecules and assuming that the concentrations \( C_X \) of donor \((X = D)\) and acceptor \((X = A)\) remains always much smaller than 1 (i.e., population of the excited state always negligible w.r.t. the ground state)

\[
FE = \frac{I}{I_0} = \frac{\sum e_{\alpha}^{\text{abs}} \Gamma_{\alpha}^{\text{rad}}}{\sum e_{\alpha}^{0} \Gamma_{\alpha}^{\text{rad,0}}} \tag{1}
\]

where the subscript “0” indicates that the quantities are referred to the case without the metal, and the sums run over the number of acceptor molecules in the system. In the above equations and in the following ones, the physical quantities of interest, which govern the population and decay of a molecular excited state \( i \), are the absorption coefficient, \( \Gamma_{\alpha}^{\text{abs}} \), the radiative decay rate, \( \Gamma_{\alpha}^{\text{rad}} \), the nonradiative decay rate, \( \Gamma_{\alpha}^{\text{rad,0}} \), the excitation energy transfer rate toward a state \( j \) belonging to a different chromophore, \( k_{\text{EET}}^{\alpha \beta} \), and eventually the rate of internal conversion into a state \( l \) of the same chromophore, \( k_{\text{IC}}^{\alpha \beta} \). For the definitions of the above quantities and the computational tools used to compute them, we refer to our previous works\(^{30,31}\) and to the Supporting Information.

**The Direct Process.** For the direct process, in which the first CHL excited state (labeled as \( Q_1 \) here and in the following) acts as both absorber and emitter of the impinging radiation, the metal-induced fluorescence enhancement becomes

\[
FE = \frac{\sum_{l=1}^{2} e_{Q_1}^{\text{abs,0}} \Gamma_{Q_1}^{\text{rad,0}}}{\sum_{l=1}^{2} e_{Q_1}^{0} \Gamma_{Q_1}^{\text{rad,0}}} \sum_{j=1}^{2} \frac{\Gamma_{Q_1}^{\text{rad}}}{(\Gamma_{Q_1}^{\text{rad}} + \Gamma_{Q_1}^{\text{rad,0}})} \Gamma_{Q_1}^{\text{rad}} \frac{\Gamma_{Q_1}^{\text{rad}}}{(\Gamma_{Q_1}^{\text{rad}} + \Gamma_{Q_1}^{\text{rad,0}})} \tag{2}
\]

where the superscript \( l = 1, 2 \) refers to the two CHLs of the system (CHL601 and CHL602, respectively). In the case of a single subdomain, containing only one CHL molecule, the above formula simplifies to the usual expression (defined as relative brightness, or RB, in our previous works\(^{31,32}\)) of a metal-chromophore aggregate

\[
FE = \frac{\Gamma_{Q_1}^{\text{rad}}}{\Gamma_{Q_1}^{\text{rad,0}}} \frac{\Gamma_{Q_1}^{\text{rad}}}{(\Gamma_{Q_1}^{\text{rad}} + \Gamma_{Q_1}^{\text{rad,0}})} \tag{3}
\]

See the Supporting Information for a detailed description of the kinetic model used to derive eq 2.

In Figure 2a–c, we report the fluorescence enhancement of the direct process for different setups, based on a single metal aggregate (of different shape) and two coupled aggregates. In the latter case, the PCP has been assumed to be placed in between the two aggregates. In all cases, the distance is defined in terms of the NP surface and the Mg atom of the selected CHL (see Figure 2a). For this first analysis, we have oriented the PCP so to have the transition dipole of the \( Q_1 \) transition in the CHL of the selected monomeric unit parallel to the long axis of the NPs.

The obtained results show a clear correlation between the plasmonic resonance and the amplification of the fluorescence. Single, elongated aggregates, which present plasmonic resonances at higher wavelengths (Figure 1e), are able to amplify the fluorescence of the system by up to a 20-fold increase. A similar increase is found for the two radiative processes with the absorption step amplified more than the emission one, which occurs at a wavelength further away from the metal resonance. Both the radiative and the nonradiative rates decay very rapidly as the metal–chromophore distances increase. Nonetheless, the nonradiative processes at short distances are found to be independent of the shape of the metal aggregate (Figure 2c,d), so that the overall trends in the fluorescence enhancements for single aggregates are determined by the different enhancements of the radiative steps (absorption and emission). When the LH complex is placed in between metal aggregates, fluorescence is enhanced by several orders of magnitude. Such a strong amplification cannot be described simply as the sum of effects of the two metal aggregates but is due to the high nonlinear
increase of the electric field at the position of the LH complex with the formation of the so-called hot spot (see Supporting Information for more details). Also in this case a clear trend can be extracted from the simulations: more elongated aggregates are found to be more effective in enhancing the radiative processes with T aggregates showing fluorescence amplifications by up to 4 orders of magnitude.

On the contrary, nonradiative decay rates are found to be almost independent of the type of the metal aggregates. Overall, the strong amplifications of the radiative processes more than compensate the nonradiative decay channels, so that a monotonic decreasing trend is found for the fluorescence enhancement of all coupled aggregates as a function of metal–PCP separation with maximum amplifications at the contact distance that corresponds to metal–CHL separations of the order of at least 2 nm (we have to take into account that the pigments are inside the protein matrix). Moreover, the presence of the embedding protein should be sufficient to prevent close associations between CHL and silver particles that could lead to quenching mechanisms due to photoinduced electron-transfer to the NPs.33,34

The proximity of the plasmonic resonance to the absorption/emission wavelengths of the CHLs can be used to rationalize the obtained trends; more elongated aggregates placed in close proximity show resonances at higher wavelengths, for example, closer to those of the analyzed processes. It is important to

Figure 3. EET-mediated process. (Top left) Visualization of the multiscale model: all the calculations have been done with the four PIDs and the CHL (VDW representation) of the selected monomeric domain described quantum-mechanically and the minimum environment (licorice) treated classically in terms of charges and induced dipoles. Only for selected points (indicated as small circles in the graph) we have extended the classical environment to include the full protein matrix (glass surface). As in the previous analysis, the distance is defined in terms of the NP surface(s) and the Mg atom of the selected CHL. (Top right) Schematic diagram of the involved processes with their characteristic decay rates: absorption is mediated by the three lowest bright (S2) excitonic states of the PIDs (S2), while the EET may occur via two different paths which involve the S2 and the dark S1 PID states, respectively (see Supporting Information). Bottom panels: results on isolated (a–c) and coupled (d–f) aggregates: (a,d) metal-induced enhancements of CHL fluorescence; (b,e) absorption amplification of the lowest three S2 excitonic states of the four coupled PIDs; (c,f) amplification of the radiative decay rates for the uncoupled PID S1 states.
stress the fact that the range of studied configurations includes cases which are very unlikely to happen spontaneously in standard experimental setups. In particular, the exact alignment of the CHL molecule with respect to the main axes of the metal aggregates is crucial for the shown amplification. As reported below, a statistical averaging of the fluorescence enhancement for the different orientations would reduce the maximum amplification (for the spherical NP a rescaling factor of 0.4 is found). Moreover, the highest enhancements are obtained at contact distances between the protein and the metal particle, which are unlikely to happen in the reported experimental conditions. From the obtained trends, it is possible to interpret the experimental results as representative of the configurations of single aggregates and of coupled aggregates at moderately large (15–30 nm) interparticle distances. Finally, we note that for the modeling of the direct process, a minimal environment is sufficient to reproduce the effects of the full protein (see the circles reported in Figure 2b–e).

The EET-Mediated Process. With respect to the direct process, in the EET-mediated process the absorbing and the emitting pigments are different and an intermediate energy transfer step has to be considered (see Figure 3 top right panel). The EET from PID to CHL is known to involve two channels, one from the PID absorbing (S1) and the other from the PID dark (S1) state, which is populated by internal conversion. As no direct estimate of the speed of internal conversion is accessible to computations, the two extreme cases of very fast and very slow S1→S1 internal conversion have been modeled, corresponding to the S1 and S2 pathways addressed in the following discussions and in the figures. As for the acceptor molecules, EET is known to occur by involving both the first (Qx) and the second (refers to as Qy) CHL excited states, followed by a very fast Qy→Qx internal conversion. As a matter of fact, among the four different EET channels, the S1→Qx one is known to be the dominant.

To simulate the EET processes, we have considered the S2 states of the four peridinins in each domain as a single excitonic system due to their very compact arrangement with PID–PID distances of the order of 4 Å. The consideration of the interactions among PIDs leads to a change in the absorption spectrum with a shift of the resulting excitonic states toward the red-edge of the band, that is, closer to the excitation wavelength used in the experiments (see Figure 1d). Since the experimental excitation energy falls at the bottom of the PID spectrum (532 nm), only the lowest-lying of the S2 excitonic states are assumed to mediate the absorption process. In our kinetic model, the first N excitonic states of the system are populated, depending on the proximity of the states energy with respect to the energy of the exciting radiation. For N = 3, results on the single domain (PID611-614 CHL602) and on the whole complex were found to be in very good agreement, thus we considered N = 3 and the single domain framework in most of our calculations. Inclusion of the fourth excitonic state (N = 4) was considered for the study of orientation effects, where the explicit treatment of the whole chromophoric complex was performed.

Contrary to the excitonic nature of the S2 states, in our kinetic equations the dark S1 states have been assumed to be uncoupled. Indeed, as evinced by highly accurate QM calculations, the S1 transition dipole of a solvated PID is within a factor of 2–3 smaller than the corresponding S2 transition dipole, depending on the polarity of the solvent. As the S1 states are populated by internal conversion, all of them need to be considered in the kinetic equations. Finally, as the couplings between the two CHLs are negligible, they can be treated in our kinetic model as separate acceptors/emitters.

Following the above assumptions, the kinetic equations for the whole system can be derived as reported in the Supporting Information for the two considered S1 and S2 pathways. In particular, for the modeling of the single domain, the concentration of the CHL601 Qx state to be introduced in the general eq 1 for fluorescence enhancement (FE) becomes

\[
c_{Q_{y}} = \frac{1}{\Gamma_{Q_{y}} + \Gamma_{rad}} \cdot \sum_{i=1}^{8} \frac{k_{EET}^{\text{abs}}}{S_{y}} \cdot \sum_{j=1}^{N} F_{y} \cdot \sum_{i=1}^{N} \frac{k_{EET}^{\text{abs}}}{S_{y}}
\]

for the S1 pathway, and

\[
c_{Q_{x}} = \frac{1}{\Gamma_{Q_{x}} + \Gamma_{rad}} \cdot \sum_{i=1}^{8} \frac{k_{EET}^{\text{abs}}}{S_{x}} \cdot \sum_{j=1}^{N} F_{y} \cdot \sum_{i=1}^{N} \frac{k_{EET}^{\text{abs}}}{S_{x}}
\]

for the S2 pathway, where the factors

\[
f_{y} \equiv \frac{k_{\text{IC}}^{Q_{y}}}{\sum_{i=1}^{8} k_{\text{IC}}^{Q_{y}}}
\]

can be recovered from the site population of each S2 excitonic state, and for a sake of brevity we have defined \[k_{EET}^{Q_{x}} = k_{EET}^{Q_{y}} + k_{EET}^{Q_{y}}\].

In Figure 3a–c, we report the distance dependence of the fluorescence enhancement for the two EET channels in different PCP–NPs setups. Also, in this analysis we have oriented the PCP so to have the transition dipole of the Qx transition in the CHL of the selected monomeric unit parallel to the long axis of the NPs.

The obtained results show that the clear monotonic trend found for the amplification of the direct process as a function of the NP type is not reflected in the EET-mediated process, where the D aggregates (instead of the T aggregates) are found to be the most effective. As the last step of the process, that is, the CHL emission, is the same for the EET-mediated and the direct processes, the differences in the trends are to be searched in the different population mechanisms of the chlorophyll excited states. Absorption of the PID excitonic states is, indeed, found to depend in a nontrivial way on the shape of the metal aggregates. Also, in this case the plasmonic properties of the aggregates (Figure 1e) allow rationalizing the obtained trends, as the coupled D aggregates show a resonance at the wavelength corresponding to the considered absorption process (532 nm). It is important to stress that the transition dipoles of the PID excitonic states are along different directions that do not coincide with the main axis of the metal NPs. The PIDs’ radiative decay channel and nonradiative transfer to NPs are also sensitive to the type of metal aggregates; their amplification is larger for larger aggregates. On the contrary, the EET step is only at the shortest metal NPs; maximum deviations of the order of 10% are found and maximum deviations of the order of 10% are found and maximum deviations of the order of 10% are found.

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the enhancement of the EET-mediated process is larger than the direct one. In all the other cases, a less efficient plasmon control on the population of the CHL excited state is obtained, which results in a lower overall fluorescence enhancement compared to the direct process, in line with experimental results. This is particularly important for the single spherical particle, where a quenching of the CHL fluorescence is found at any metal-PCP separation for the selected orientation analyzed.

The experimental fluorescence intensity of single PCP complexes on a SIF shows for the EET-mediated process enhancements up to a factor of 18 with an average amplification factor of 6 and a noticeable fraction of quenched complexes. Similarly to what was found for the direct process, these results are compatible with the experiments, which show enhancements up to a factor of 4 for isolated metal aggregates and up to a factor of 25 for pairs of metal aggregates at moderately large (15−30 nm) interparticle distances. A statistical average over a random distribution of distances and orientations would allow a direct comparison with the amplification factors obtained from ensemble fluorescence and will be the subject of future studies. Nonetheless, by considering that the reported results for the EET-mediated process are less sensitive to orientation statistics, compared to the direct process (as reported in the following), our computational approach correctly identifies the EET-mediated process as the least prone to metal-induced amplification, in remarkable agreement with the average enhancement factor of 8.5 observed for the direct process.

Finally we note that for the modeling of the EET-mediated process, a minimal environment is still qualitatively sufficient to reproduce the effects of the full protein as found for the direct process (see the circles reported in Figures 3b−f). Here, however, some differences are found due to the effects that the full protein has on the excitonic description of the peridinins.

**The Full Interacting System.** In all previous results, we have assumed a single domain (4 PIDs and 1 CHL) frozen in a selected orientation with respect to the NPs. Now we further increase the realism of the simulation by introducing orientational averaging effects as well as by extending the description to the entire PCP monomer. In this analysis, we have two emitting CHLs and 8 donor PIDs. According to our calculations the CHL−CHL distance of about 17 Å is long enough to prevent significant couplings between the two chlorophylls that can be seen as independent molecules. On the contrary, interdomain edge-to-edge distances between PIDs...
are in the range of 4–11 Å, that is, they are close enough to have significant excitonic effects. Here such effects are taken into account by considering the complete excitonic system made of eight interacting PID; as shown by the resulting absorption spectrum (see Figure 1d), of the eight excitonic states only the four more red-shifted are in proximity of the excitation wavelength and only these will be included in the following analysis of the EET-mediated process. In order to simplify the analysis of the results, only the single spherical particle has been modeled explicitly. The metal–CHL distance has been chosen to be in the range of maximum amplification of the direct process for the single orientation considered in the above analysis (namely ca. 11 nm).

The results are reported in Figure 4a–c and show that orientation can play a crucial role in the overall efficiency of the hybrid device.

In particular, a dramatic effect is reported for the direct process (Figure 4a) where a significant fraction of the possible orientations show a large quenching of the chlorophyll fluorescence, while optimal configurations present amplifications up to a factor of 2 with respect to the isolated PCP complex. The presence of two chlorophylls allow for a more homogeneous distribution of amplifications along the possible orientations with the maximum corresponding to the metal particle placed along the axis bisecting the two Y-axes of the individual chlorophyll molecules (identified by their Q_y transition dipoles). Such an orientation is indeed able to significantly populate the Q_y excited states of both chlorophylls.

A more complex behavior is found for the EET-mediated process (Figure 4b,c), which is found to be more selective to plasmon-controlled amplification. The highest amplification (of about 2) is found for a NP which is somehow displaced from the two chlorophylls Y-axis and their average. Such a configuration is thus the result of a compromise between the amplification of the PID excitonic absorption and the CHL emissions. As the EET couplings are not significantly affected by the metal orientation, they only act as selector of the preferred channels for the transfer of excitation energy. It is thus probable that orientations that result in high amplifications of one of the PID excitonic states would only be able to populate one of the two CHLs excited states. The important point to notice is the strategic role of the complexity of multichromophoric bundles in making the LH process sensitive to the environment in an averaged way. In a system that involves several processes (i.e., absorption, EET, and emission), which occur at different wavelengths and involve transition dipoles oriented in different directions, it is possible to enhance even by orders of magnitude, one of the steps. On the other hand, while the presence of several channels allows different, equally effective, amplification strategies, optimal amplification of all the steps at once is less trivially achieved. This is reflected in more homogeneous, but generally less intense, amplification effects in the EET-mediated process, compared to the direct one.

The results obtained so far allow us to go further and to propose some rules to guide the design of LH biohybrid devices based on PCP and silver NPs. Such biohybrid devices are aimed at capturing a large portion of the sun spectrum and transfer the stored energy either to the biological partner (reaction centers) or to other artificial photovoltaics organic or inorganic components tuned to exploit the CHL emission. Both the direct and EET-mediated processes should be enhanced to exploit the largest part of the sun spectrum. The design rules are the following:

1. **Single-particle versus hot-spot geometry.** The largest fluorescence enhancement for both processes (10^4–10^5 for direct, 10^4–10^5 for EET-mediated) is obtained for PCP in a hot-spot. Therefore, this should be the preferred NP–PCP geometry. Nevertheless, PCP interacting with single particles also provides useful enhancement and may represent a simpler building paradigm for devices.

2. **PCP–NP separation.** For the hot-spot geometry, the direct process is maximized for PCP as closest as possible to the NP (Figure 2d), while the EET-mediated process is optimal when a distance of ~1–2 nm is separating the NP and the PCP (Figure 3e). Considering that PCP in contact with the NP may undergo unfolding, 1 nm seems to be an overall good choice which corresponds to about 4 nm separation between the metal particle surface and the pigments. For the single-particle setup, the range of PCP–NP separations where the fluorescence is maximized is around 7 nm both for the direct and the EET mediated processes, and it is also not greatly affected by the particle shapes (Figures 2a and 3a).

3. **PCP–NP relative orientation.** The analysis performed for the single-particle geometry (Figure 4) has shown that the direct process is quite sensitive to the PCP–NP orientation. This is to be expected also for hot-spot geometry, as the enhanced field is highly directional in the hot-spot. Therefore, correctly orienting PCP is an important requisite to take full advantage of the plasmonic enhancement on the whole sun spectrum, although for the EET-mediated project the requirement is less stringent as discussed above.

4. **Illumination and emission geometry of the PCP–NP system.** For all the processes, the maximum enhancement is obtained with an illumination with light polarized along the direction of the largest elongation of the aggregates. Emission is dipole-like with the emitting dipole also oriented along the major axis of the NP. The system that receives the PCP–NP energy should be placed taking into account the anisotropy of such dipolar emission.

As a complement to these four main rules, it is worth recalling that a relevant issue in designing optimal devices is the absorption of light by the nanoparticles. In fact, in the limit where the volume of silver becomes too large with respect to the volume of pigment molecules, metal absorption is likely dominating. Yet, the calculated magnitude of the enhancement (up to 10^5–10^6), together with the possibility of choosing nanoparticles whose absorption has the least overlap with pigment absorption and emission, makes us confident on the feasibility of using PCP–NP as an efficient light-harvester.

In conclusion, the analysis reported above clearly indicates that QM-based multiscale simulations represent a fundamental tool to deeply understand the delicate balance of competitive processes that finally lead to the enhancement of fluorescence in LH systems placed in proximity of metal NPs. Only by combining QM descriptions with classical but polarizable models for both the molecular and the nanoscopic environment, it has been possible to reveal how, in each of the involved processes, the electronic characteristics of the pigments as well as the properties of the local environment are differently coupled to the surface plasmons. In addition to allowing a complete interpretation of experiments, the application of accurate QM-based multiscale approaches in which all the components are taken into account with their specific physical–chemical characteristics can be exploited to infer
and the EET-mediated process. Values of EET couplings and rates as well as metal effects on radiative and nonradiative decay rates. Plots of metal-induced field enhancements for selected setups. All results on the extended model. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES**


