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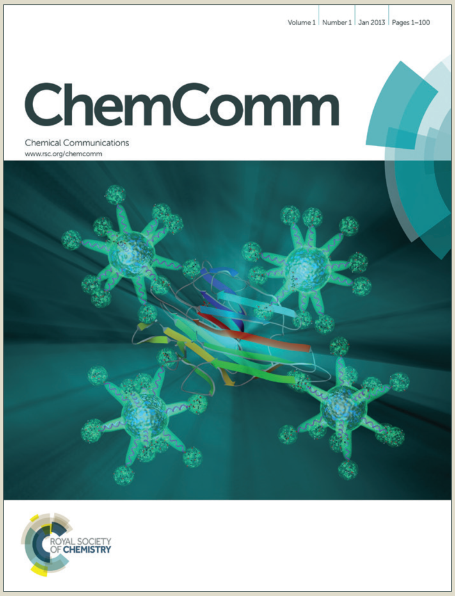

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Artificial light-harvesting arrays for solar energy conversion

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Solar fuel production, the process whereby an energy-rich substance is produced using electrons provided by water under exposure to sunlight, requires the cooperative accumulation of multiple numbers of photons. Identifying the optimum reagents is a difficult challenge, even without imposing the restriction that these same materials must function as both sensitiser and catalyst. The blockade caused by an inadequate supply of photons at the catalytic sites might be resolved by making use of an artificial light-harvesting array whose sole purpose is to funnel photons of appropriate frequency to the active catalyst, which can now be a dark reagent. Here we consider several types of artificial photon collectors built from fluorescent modules interconnected via electronic energy transfer. Emphasis is placed on the materials aspects and on establishing the basic operating principles.

Introduction

Photosynthesis provides the essential chemical energy for almost all life on Earth and has done so for more than two billion years. The initial step in photosynthesis concerns absorption of sunlight to generate excitons localised on peripheral antennae assembled from a limited variety of chromophores. These excitons migrate around the antenna,[1] moving between seemingly identical clusters in an apparently incoherent manner,[2] until trapped at a reaction centre complex where electron transfer occurs.[3] It is important to appreciate the fact that an effective light-harvesting array is essential for the proper functioning of photosynthesis. Nature uses many different molecular architectures, each designed for a specific purpose, and takes immense care to arrange the individual components in a precise fashion that permits collection of all excitation energy within a desired frequency range and facilitates long-range migration of the excitons with mimimum loss.[4] This latter step, which might involve excitation energy transfer over large distances or between several hundred chromophores, must be rapid in order to compete with the inherent deactivation of the exciton. Tremendous progress has been made in terms of understanding the function, energetics, dynamics and structure of photosynthetic light-harvesting arrays, although important issues[5] still remain unresolved. The major molecular principles have been identified at sufficient levels of understanding to allow the formulation of artificial analogues that could advance our attempts to devise new strategies for solar fuel production. It is the purpose of this review to establish the state-of-the-art in terms of artificial light-harvesting networks and to direct attention to areas where further research seems necessary.

The architecture and composition of natural antenna complexes vary remarkably among the different organisms and, as in the DNA photolyase repair enzyme,[6] can be very simple in both structure and function. The main purpose of such arrays is to collect excitation energy above a certain threshold and direct this excitation to a particular site where irreversible chemistry takes place. Mostly, the chemical reactions are based on electron transfer – as in DNA repair[6] – and one critical function of the photon collector is to maintain a steady supply of excitons to drive the chemistry in the preferred direction. This simple concept is extremely important in terms of multi-electron catalysis, such as water oxidation in green plants,[7] because free-radical intermediates cannot be easily controlled if left unattended for a few seconds. The rate of oxygen evolution by green plants, for example, under ambient conditions is of the order of 30 μmol per m^2 per second.[8] This could not be achieved without an effective light-harvesting component. A further advantage of this basic strategy is that the actual catalyst does not need to be strongly coloured, thereby overcoming a major limitation in respect of the choice of materials, while the ancillary electron-transfer reagents need only set the threshold energy without the need for them to absorb over a wide frequency domain. An intriguing feature of natural analogues, and an important concern for artificial devices, is that the photon collector can be repaired without dismantling the active catalytic site.

Related functions accomplished by the light harvester include demoting high-energy UV photons, avoiding exciton overload, redirecting excitons as required and eliminating concentration quenching (i.e., self absorption or aggregation) while collecting all incident sunlight. Obviously, the arrays have to be cheap to assemble, relatively stable, easily adaptable and self repairing. These are nontrivial functions that present massive challenges to the molecular chemist regarding their duplication in the laboratory. For example, the closest centre-to-centre distance between bacteriochlorophyll molecules in protein arrays is ca. 10 Å,[9] corresponding to a local concentration of ca. 0.1 M. In contrast, chlorophyll in diethyl ether solution suffers catastrophically from self-absorption at concentrations above ca. 100 μM.[10] This highly compact packing, which is facilitated by the protein scaffold, must be built into the artificial analogues but the best way to do this is far from obvious. Likewise, the problems arising from self absorption, which cannot be overcome with a cocktail of individual dyes, should not be underestimated!

It is not necessary to duplicate all the features inherent to photosynthetic light-harvesting arrays since our needs differ and are not as stringent as in the natural world. In particular, it seems inappropriate to focus exclusively on bio-inspired chromophores, such as porphyrins, and to operate only with protein-bound materials. Nonetheless, we have to learn from the natural systems and engineer robust arrays able to operate over extended surface areas and to perform valuable tasks. Attention is drawn now to two disparate photosynthetic light-harvesters that serve as templates for artificial devices. These systems, deliberately selected because of their apparent lack of complementarity, are the Fenna-Mathews-Olson (FMO) protein trimer from green sulfur bacteria[11] and the unusual phototrophic bacteria that inhabit the South Andros Back Holes.[12]

The FMO complex (Figure 1) is an acretion of three identical subunits, each comprising seven bacteriochlorophyll-a molecules enclosed in β-sheets.[11] Interactions with the surrounding protein give each pigment a unique spectroscopic signature. The nearest centre-to-centre separation distance is ca. 11 Å for pigments in the same subunit and ca. 24 Å for inter-subunit chromophores. The complex acts as an excitation energy bridge for electronic energy transfer (EET) from the peripheral light harvesters to the reaction centre complex (Figure 1). The close proximity and energy tuning via protein coordination favours the strong coupling between pigments that allows highly directional EET to the reaction centre. Recent studies[13] using 2D absorption spectroscopy have implicated quantum coherence[14] as playing a role in the EET mechanism. In our artificial world, the FMO complex would couple a photovoltaic cell to a large panel solar concentrator (Figure 1).

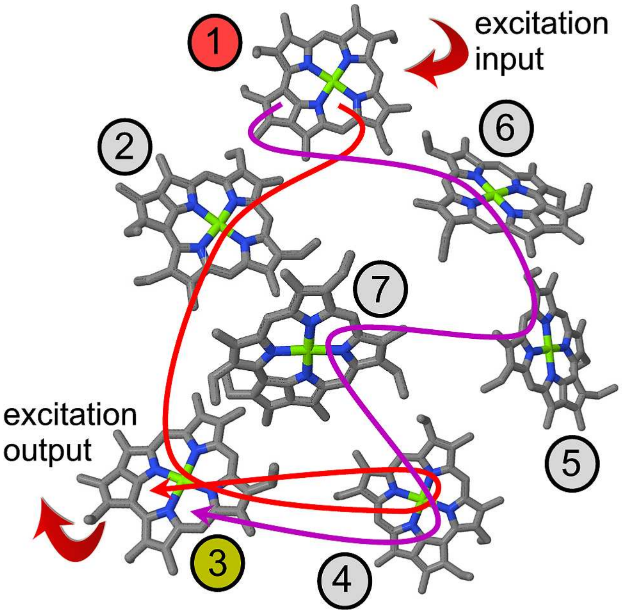

Figure 1. Simplified scheme showing the EET pathways inherent to the FMO complex that links the light-harvesting complex to the reaction centre. The two EET paths are indicated by red and plum lines.

The South Andros Black Hole[12] is a land-based cavity, filled with water, playing host to an intriguing mass of purple sulfur bacteria that operates as an efficient heat engine. These bacteria contain high concentrations of diverse carotenoids which perform quite poorly in terms of EET and convert the excitation energy into local heat.[15] The mass of bacteria, comprising a dense layer of ca. 1 m depth, maintains the external temperature at 36 °C, which is sufficient to deter predators whilst favouring growth of the phototrophs. Energy transduction of this type has great relevance for solar energy conversion in Northen Europe where the major energy demand is for domestic heating. The artificial analogue (Figure 2) would provide input during the daytime to a heat exchanger or catalytic cycle that could be used to store chemical energy until released during the night. There are, in fact, many photochemical cycles[16] that could serve this purpose but no attempt has been made to equipe the photoreactor with an ancillary solar concentrator of the type considered here.

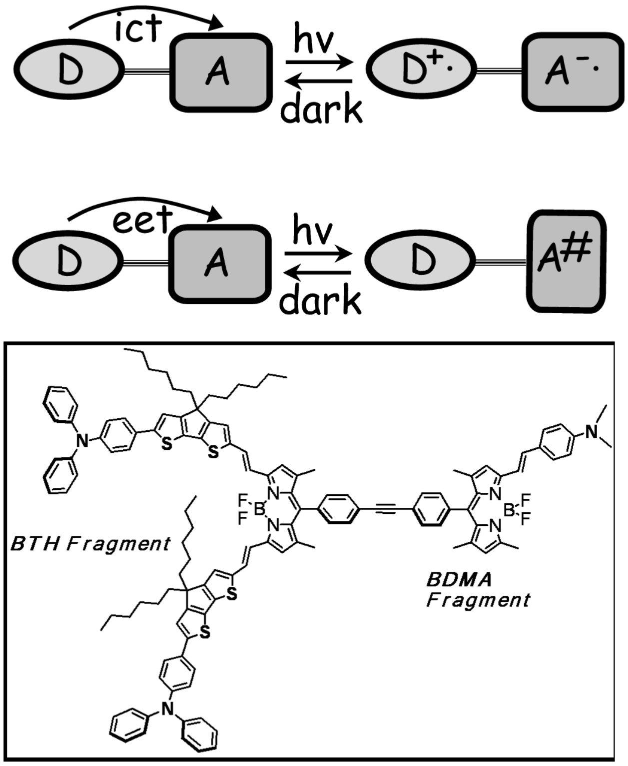

Figure 2. The upper panel shows a representation of the types of photochemical schemes that could duplicate the essential features of the phototropic bacteria which operate as heat engines in the South Andros Black Holes. The lower panel provides an example of a molecule able to convert excitation energy into localized heat via light-induced charge transfer.

Molecular design

No single chromophore possesses a suitable optical absorption spectral profile to enable efficacious collection of sunlight over the range 300 to 800 nm; we use this spectral window as illustrative of what needs to be accomplished rather than as a definitive demand. Several disparate chromophores are needed, each being responsible for harvesting a certain wavelength domain, in a way reminescent of certain cyanobacteria (Figure 3).

Now, the compounds have to be assembled in a logical manner that permits rational EET between the individual chromophores. We will not consider the EET mechanism, except in a cursory manner,[†] since this is better treated in more specialised journals, but limitations mean that neighbouring chromophores must reside within ca. 50 Å and that a modest fraction (i.e., 5%) of the excitation energy must be lost to ensure fast, directed EET. There must also be adequate spectral overlap between fluorescence from the energy donor and absorption by the respective energy acceptor (Figure 3) in order to drive one-way EET. Other factors, such as mutual orientations and inter-connecting bridges, are less important at this stage. Even so, there are several ways in which the subunits can be joined by way of covalent linkages; generic categories can be identified as (i) directly coupled, (ii) dendrimer-based and (iii) scaffold assembled. According to the nature of the chromophores, various EET steps can be envisioned among the assembled clusters, as outlined in Figure 4.

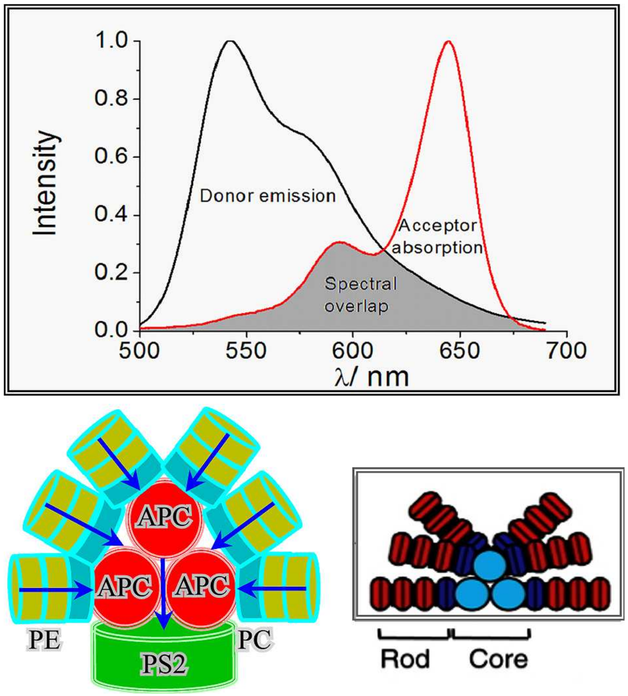

Figure 3. (Upper Panel) Example of the spectral overlap that plays a critical role in determining the efficiency of excitation energy transfer. (Lower Panel) Representation of the EET steps (blue arrows) inherent to cyanobacteria, where PE refers to phycoerythrin, PC refers to phycocyanin, APC refers to allophycocyanine and PS2 refers to photosystem-2.

It might be mentioned that only spasmodic attention has been given to selecting the optimum geometry for an artificial solar concentrator.[17] Of the designs shown in Figure 4, the linear arrays are of least significance because they are rendered next to useless if one component becomes damaged during operation. Zig-zag arrangements are less prone to such disastrous damage since they can by-pass certain EET steps if necessary. V-Shaped structures have an in-built redundancy that leads to robust arrays and also provide multiple routes for the excitation to reach its ultimate destination. Dendrimers[18] overcome many of the synthetic difficulties associated with constructing ordered arrays but suffer badly from poor directionality. Thus, it is straightforward to direct excitons to the centre or to the periphery but impossible to send the exciton to one particular chromophore on the outer surface. The use of scaffolds to position chromophores at predetermined locations solves many problems and provides an interesting alternative to the design of V-shaped arrangements. In all cases, however, it is necessary to identify complementary chromophores that act cooperatively to collect a large fraction of the solar spectrum and that impose the required energy threshold.

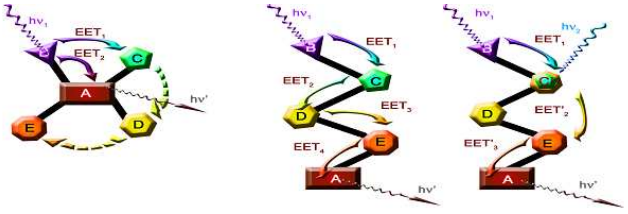

Figure 4. Examples of the type of molecular architectures that might be used to fashion artificial light-harvesting antennae displaying certain elements of redundancy. Each system is based on the use of a series of dyes to cover the entire visible spectral range and directed EET between the dyes and finally to the ultimate acceptor, A.

Regardless of the actual design, it is clear that some quite elaborate synthetic chemistry will be needed to construct suitable edifices, even at the laboratory scale. Before attempting to do so, it seems prudent to enquire if there is a genuine advantage from using tailored multi-component arrays in place of the isolated reagents. Random dispersions of chromophores are never going to provide for the necessary directionality and are likely to enter into undesirable quenching events such as aggregation and light-induced electron transfer. Moreover, even with fractal dimensions, multiple layers of chromophores are needed to achieve optimum levels of light absorption. There is also the question of photo-stability of the dyes,[19] bearing in mind that it is extremely difficult to protect organic dyes against degradation in strong sunlight. A marked feature of the synthetic arrays, as in natural photosynthesis, is that, because of fast EET, the excited states of participating chromophores are too short to enter into deleterious photochemical reactions. As such, damage is restricted to the terminal acceptor[20] and this site can be repaired by *in situ* treatment.

Assuming the light harvester works according to the design element, incident sunlight will be collected across the array and channeled to the terminal acceptor by a series of EET events. The terminal will fluoresce in the absence of a coupled device, such as a solar cell, or undergo EET so as to activate the device when the latter is in place. Now major problems emerge in terms of materials science. Firstly, it is necessary to connect the device and light harvester in such a way that no EET barrier is imposed and without switching on undesirable quenching events. Secondly, a large number of light harvesters must be attached to a single device in order to produce a viable effect. In photosynthesis, for example, there is one reaction centre complex for every 250-400 ancillary pigment molecules.[21] The use of plastic solar concentrators, itself an active research field,[22] offers a relatively simple solution to the second issue but is outside the scope of this article. We will return to this crucial design feature at a later point.

Bichromophoric systems

As a means by which to introduce the field, we will focus on two simple systems that serve to illustrate the types of EET events occurring in molecular constructs. In fact, intramolecular EET in molecular dyads has been studied in great detail over several decades in order to learn about the underlying mechanisms, especially in terms of how the rate varies with molecular length.[23] Flexibly-linked molecular dyads do not help in this respect since the dynamics of chain motion are competitive with the rate of EET and it has proved necessary to synthesize rigid molecules bearing active terminals. Representative of such molecules is the series of boron dipyrromethene (Bodipy) dyads[24] shown in Figure 5. Here, the disparate terminals, both being highly fluorescent Bodipy dyes but with differing conjugation lengths, favour rapid EET along the molecular axis. The connecting unit is a conjugated alkyne-based bridge that acts as a collector for near-UV photons. Long-range EET between the terminals, which is primarily a through-bond process[25] despite the orthogonal linkage at the donor site, is essentially quantitative but the dynamics can be followed by time-resolved emission and transient absorption spectroscopy. This rate is unaffected by increasing the length of the bridge, at least to 40 Å, or by lowering the temperature.[24] A further point of importance is that rapid EET occurs in the solid state. Such studies help refine our understanding of the role of the bridge and how to construct longer molecules without curtailing the EET process. The systems displayed in Figure 5 operate via the singlet-excited state but related work has confirmed that much the same situation holds for triplet-state processes.[26] Here, the terminals comprise phosphorescent transition metal complexes and the work has relevance for the design of next-generation OLEDs, especially in terms of identifying white-light emitters.

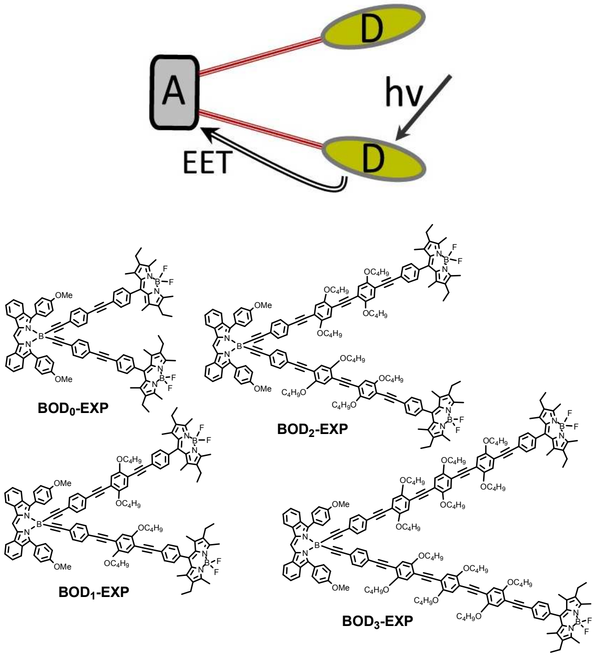

Figure 5. Examples of molecular dyads developed to test the distance dependence for EET. The numeral subscript refers to the number of interspersed 1-ethynyl-2,5-dibutoxyphenyl subunits in the spacer unit.

This distance-independent EET is in sharp contrast to what happens when the bridge does not participate in super-exchange interactions. Now the rate of EET falls dramatically as the separation distance increases, as has been demonstrated[27] for the series of *para*-carborane bridged dyads illustrated in Figure 6. It has not been easy to identify rigid bridges that span the necessary range of distances needed to effect such a study and even these structures are subjected to geometry fluctuations under ambient conditions. However, the comparison exemplified in Figure 7 is highly informative with respect to the importance of the connecting spacer.[28] This unit must be optimised for long-range EET in order to minimise undesirable loss of excitation while also contributing to the overall photon harvesting. This is a clear advantage of the molecular wires described above. It might be noted that these compounds lead to the construction of V-shaped molecules by employing the "synthesis at boron" approach.[29]

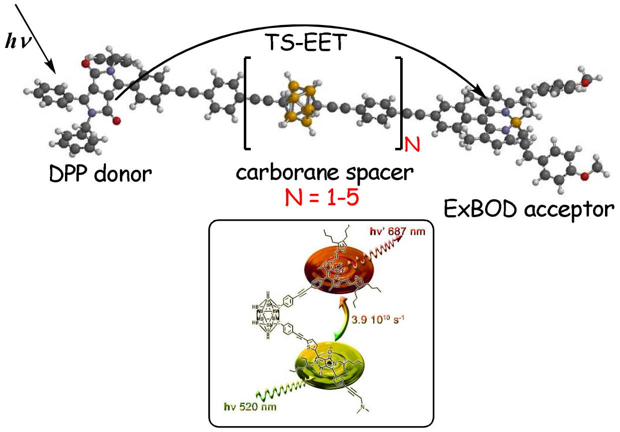

Figure 6. Molecular formula of the para-carborane bridged molecular dyads used to explore the distance dependence for through-space electronic energy transfer (TS-EET) from the diketopyrrolopyrrole (DPP) donor to an expanded Bodipy acceptor. The lower panel shows the formula for the corresponding ortho-carborane-based dyad.

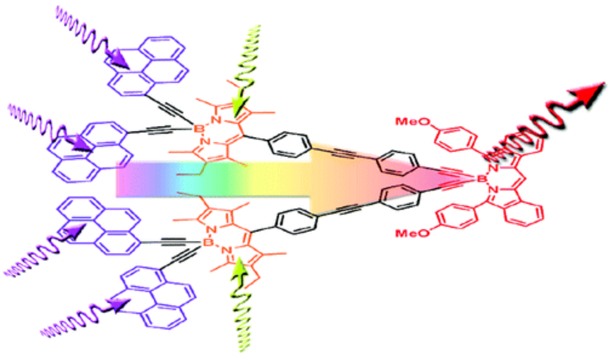

Figure 7. Illustration of EET occurring in a cascade-type molecular triad where short-range EET steps replace the long-range transfer evident for Figure 6.

A quite different molecular system, one that illustrates the versatility of the field, is generated by attaching secondary chromophores to the bowl-shaped sub-phthalocyanine (Sub-PC) residue.[30] A few representative structures, made possible using the "synthesis at boron" strategy, are shown in Figure 8. Here, illumination into the Sub-PC unit results in quantitative EET to the expanded-Bodipy terminal (Figure 8 upper panel), which fluoresces in the far-red region. Protonation of one or both amino-groups resident on the acceptor does not hinder EET but changes the wavelength of the emitted fluorescence. In fact, this output can be tuned over a wavelength range in excess of 120 nm.[30] Replacing the Bodipy dye with an osmium(II) *tris*(2,2'-bipyridine) complex (Figure 8 lower panel) changes the EET landscape. Now illumination into Sub-PC is followed by fast EET to populate the lowest-energy triplet state on the Os(II) complex. This event, which is essentially quantitative, is followed by triplet-triplet energy transfer to form the excited-triplet state localised on the Sub-PC (Figure 8). Thus, the net result is enhanced intersystem crossing for the donor, and thereby an increased propensity to generate singlet molecular oxygen under irradiation. The unique topology of the Sub-PC moiety favours complexation of C_{60}, which is known[31] to possess an unusually low triplet energy. Consequently, binding C_{60} to the dome-shaped Sub-PC results in sensitisation of the triplet state of the guest via intermediate excitation of the Os(II) complex.[30]

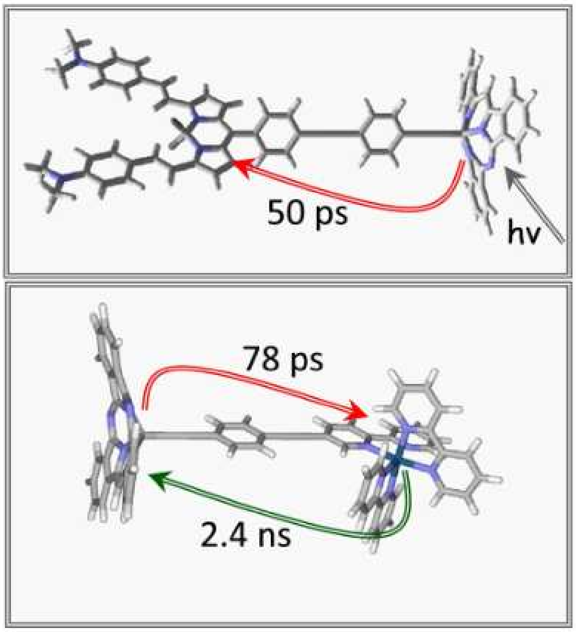

Figure 8. Representation of the EET processes pertaining to the two Sub-PC-based molecular dyads. The upper panel shows EET from the bowl-shaped Sub-PC to a nearby expanded-Bodipy dye whereas the lower panel illustrates singlet-singlet EET from Sub-PC to a covalently attached osmium(II) tris(2,2'-bipyridine) complex followed by triplet-triplet EET to the Sub-PC fragment.

Dendrimer-like arrays for photonic applications

The above-mentioned examples of intramolecular EET taking place within molecular dyads could be augmented by hundreds of related cases covering varied aspects of the field. These dyads have many important applications in analysis, signal transduction and bio-labelling, as well as playing an important role in furthering fundamental knowledge. Unfortunately, they are not especially useful light-harvesting units since they rarely collect more than 30% or so of the visible spectral range. There are additional problems relating to self-absorption and chromophore density and, in almost all cases, molecular dyads fail to fulfill the essential requirements inherent to a viable sensitiser for solar cells. Larger arrays are needed that overcome these issues and it is natural to think in terms of polymers. Indeed, a variety of polymeric backbones have been decorated[32] with chromophores that display EET along the strand. Similar materials can be assembled by intercalation[33] of fluorophores into DNA or attachment to protein helices[34] and again efficient EET has been reported over considerable distances. These intricate materials offer no real advantage over a random array of isolated chromophores embedded in an inert plastic and, in the case of polymer-bound sensitisers, are often complicated by self aggregation and conformational heterogeneity. Alternative approaches have been taken that utilise the layered structures inherent to most classes of dendrimers.

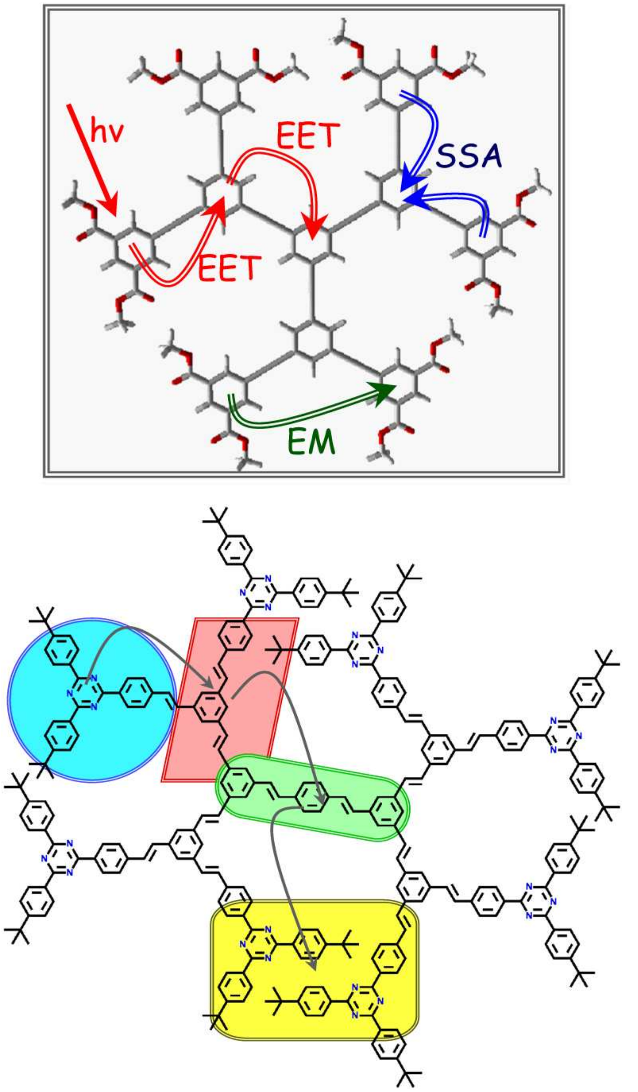

Figure 9. Illustration of EET in dendrimer-derived molecular architectures. The upper panel shows successive EET steps from periphery to core (red), singlet-singlet annihilation (SSA) at the periphery (blue) and exciton migration (EM) (green). The lower panel shows successive EET steps and illustrates the importance of excimer formation (yellow panel).

In certain respects, the structural arrangement of the pigment layers in a typical phycobilisome (Figure 3), this being the elegant light-harvesting unit present in cyanobacteria,[35] resembles a distorted dendrimer. The central unit, which sits immediately above the reaction centre complex, comprises allophycocyanin molecules. Attached to this centre are wires built from a layer of phycocyanin followed by a layer of phycoerythrin.[36] These branches serve to increase the surface area of the coloured fragments while the cascade of EET steps from periphery to interior acts to focus excitons at the reaction centre complex. The overall EET efficiency exceeds 95% and is complete within 100 ps. Incidently, this organism was probably the first such system to be examined by time-resolved fluorescence spectroscopy.[37]

Layered dendrimers, where the layers combine to give a gradient of excitation energies similar to the situation found with phycobilisomes (Figure 3), are ideally set up to explore cascade EET. Here, excitation of the core chromophore is followed by successive EET steps until the exciton reaches the periphery (Figure 9). Depending on the nature of the dendrimer,[38] and allowing for rotational motion of individual chromophores, the exciton can migrate around the surface.[39] This leads to interesting observations, such as excimer formation and exciton-exciton annihilation, that themselves lead to non-linear optical properties. Among the many fascinating photophysical examinations carried out with chromophore-bearing dendrimers, attention is drawn to the sophisticated single-molecule fluorescence studies reported by De Schryver et al.[40] This work has nicely illustrated the possibility to monitor the progress of one or two photons attached to a single dendrimer. In turn, the information so gathered has stimulated interest in developing new algorithms for predicting the course of EET around intricate molecular architectures[41] as a function of photon flux. These computer tools, taken together with advanced graphics, can simulate Förster-type EET in essentially any isotropic medium on the basis of statistical arguments.

To date, photophysical studies have been restricted to solitary dendrimers and there is a scarcity of information relating to inter-dendrimer EET. One obvious problem arising from these molecular architectures concerns the lack of directionality inherent to this type of topology. Directing the exciton to the interior will introduce undesirable anniliation steps and difficulty associated with extracting the photon by a light trap. Equipping the dendrimer with some kind of recognition facility to aid binding to the trap has not been done as yet. Reversing the direction of EET from core to periphery is likely to promote self-absorption and the ensuing defocussing of the excitation is not conduicive to efficient trapping. Thus, dendrimers remain egnimatic, at least as far as building practical photon collectors.

An interesting derivative[42] of this approach coats a naked poly(ethylenimine) nanoparticle with a layer of fluorescein isothiocyanate, which emits at 517 nm. The surface bound dye is then covered with a layer of poly(acrylic acid), to which is attached an outer coating of a spirolactam rhodamine derivative. The latter dye emits at 591 nm and functions as an acceptor for intra-particle EET from fluorescein. The probability of EET is determined, in part, by the thickness of the poly(acrylic acid) layer, although this is difficult to control with any real precision. No doubt this system could be further modified and optimised for light-harvesting potentiality. It should be noted that Samuel *et al.*[43] have neatly demonstrated the systematic scaling of the rate of EET with distance between thin films of conjugated polymers separated by a silica spacer. The EET rates followed an inverse cubed relationship with separation distances above 80 Å.

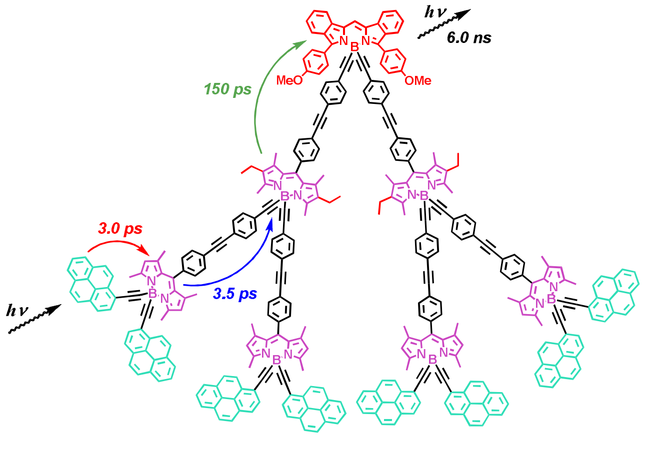

Figure 10. Molecular formula for the large artificial light-harvesting array comprising 21 discrete chromophores, with the lifetimes indicated for each of the main units.

Molecular-scale photonic wires

With reference to Figure 4, it is nowadays possible to synthesize elaborate arrays by stepwise attachment of prefabricated modules in such a way as to create a gradient of excitation levels running along the molecular axis. Such arrays are not restricted to linear geometries, although these have proven to be the most popular choice.[44] A key point of such architectures is that, by careful selection of the terminal acceptor, it is a simple matter to eliminate problems arising from self absorption. Thus, the final acceptor should either be present at relatively low loading, easily achieved with V-shaped geometries, or possess a relatively small oscillator strength for the lowest-energy absorption transition. A prototypic array, which comprises 21 individual pigments,[45] is illustrated in Figure 10. The operating principle for all such molecular networks is based around a molecular light guide wherein different chromophores are linked in a linear or branched fashion. Each chromophore absorbs a certain fraction of the solar spectrum and enters into unidirectional EET with neighbouring chromophores. In 2- or 3-D arrays, sideways EET can help overcome bottlenecks and deal with photon overload. Photons enter the array at any chromophore and travel along the energy gradient. Successful implementation of the chosen design element depends on precise positioning of adjacent chrmophores, decided on the basis of the projected EET mechanism, and on their spectral overlap integral.

This latter term[46] is of great significance since it determines how much excitation energy is lost at each EET step and indirectly controls how many disparate chromophores are needed to fill the desired spectral window. Although many photonic wires have been reported, often with detailed understanding of the rates and mechanisms of EET, it has not been possible to create a black absorber and, in many cases, substantial holes persist in the spectral coverage. The biggest problem with this approach is the rather limited stability of most organic dyes when subjected to prolonged illumination. However, for a properly designed array, only the terminal acceptor needs to be unusually photostable[47] but this particular component plays a crucial role and is likely to possess a large π-conjugation pathway which is susceptible to oxidative damage. The rate of degradation can be cut down by ensuring fast offload of the photons to some kind of device, such as a solar cell. Under these conditions, stability might be high and turnover numbers for the terminal dye in excess of 10^4 have been obtained in certain cases.[45] In this particular example, the turnover frquency is ca. 0.1 Hz.

This performance can be compared with the anticipated turnover number of chlorophyll molecules in natural photosynthesis, which is of the order of one million. The large array shown in Figure 10 has been used[45] to sensitise a solar cell, with some benefits relative to direct illumination being achieved at high photon flux. This array corresponds to a chromophore concentration of ca. 0.6 M confined to a volume of ca. 55 nm^3. The material absorbs strongly across the spectral range from 300 to 710 nm, although transparent regions appear at around 430 and 560 nm. Closely-related arrays[48] have been built from components that absorb strongly in these particular regions so that, in principle, the only barrier to improving the photon collection capacity is synthetic cost. Indeed, plastic films containing mixtures of two complementary molecular-scale arrays are able to absorb all incident light at wavelengths >700 nm. Emission is concentrated into a window around 700-750 nm. In terms of optical properties, we are now close to mimicking the leaf. Although not yet in a position to incorporate repair processes intended to heal damaged units, a certain degree of redundancy can be introduced as a means to further stabilise these arrays. It might be noted that there are many detailed compendia of photophysical properties, including absorption and emission spectra, but there are no such lists indicating the photostability of organic dyes.

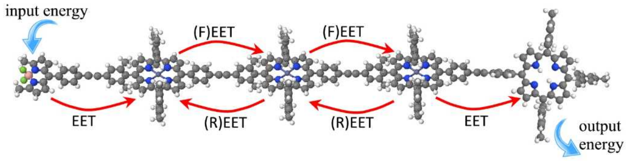

Figure 11. Prototypic molecular-scale wire, comprising a Bodipy-based dye as input unit, three zinc porphyrins capable of forward and reverse energy transfer and a terminal free-base porophyrin as the emitting output unit.

Other notable examples of molecular-scale photonic wires include the linear array of five components described by Lindsey *et al*.[49] This system comprises a Bodipy dye as in input terminal, with three identical zinc porphyrins as light propagator, and a free-base porphyrin as the output terminal (Figure 11). Absorption is fairly strong over the range 350-650 nm and some 92% of incident photons are emitted by the free-base porphyrin. This latter component is relatively stable under illumination with red light. Moreover, with minor modification of the system[50] it is possible to introduce a redox switch that provides for a certain degree of directionality. A second system, introduced by Sauer *et al*.,[51] comprises a linear sequence of five complementary chromophores spanning a length of ca. 135 Å (Figure 12). The array, which harvests light over a 200-nm window, has been attached to duplex DNA so as to ensure the extended conformation persists and the overall probability of end-to-end EET is around 90% for single molecules. Under illumination, the final acceptor bleaches successively and thereby provides a nice demonstration of the principle outlined above. Linear arrays capable of long-range triplet energy transfer[52] have been constructed from ruthenium(II) poly(pyridine) complexes and shown to operate over distances of ca. 60 Å.

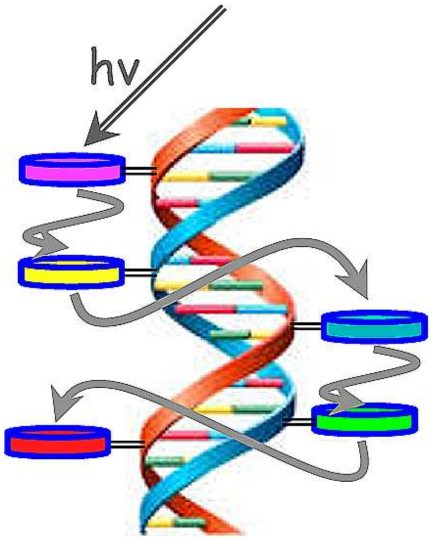

Figure 12. Illustration of a molecular-scale wire assembled around the DNA duplex. Each coloured disk is intended to represent a different chromophore arranged so as to facilitate a cascade of EET steps.

One of many intriguing aspects of natural photosynthesis is the ability of the light-harvesting complexes to adapt to certain stimulii and thereby re-direct photons around the network. It is believed that the trigger is provided by a proton gradient released at high photon flux.[53] A crude mimic of this situation has been brought about by equipping the final acceptor[54] with a readily protonated amino residue (Figure 13). Thus, illumination of the central donor (DPP) present in the neutral molecule is followed by preferential (i.e., 75%) EET to the blue acceptor (BLU). Secondary EET then occurs from BLU to the green acceptor (GRE). The reaction sequence is dictated by the respective spectral overlap integrals. Overall, some 98% of incident photons reach the green acceptor within 100 ps of excitation. On protonation of the green acceptor, EET from DPP now proceeds preferentially (i.e., 60%) to GRE and is followed by long-range EET (i.e., 34 Å centre-to-centre distance) from GRE to BLU. Thus, the EET direction is reversed, and again essentially all incident photons reach the blue acceptor within a timescale of 40 ps. A novel feature of this system[54] is that the protonation step can be engineered by separate illumination of a photoacid, the entire reaction being driven in a plastic film.

In passing, it seems appropiate to compare these molecular-scale photonic wires with the state-of-the-art silicon wire waveguides[55] that feature very strong optical confinement and compliance with silicon-based electronics. The fundamental propagation performance of these waveguides has already become a practical standard and has enabled the development of certain passive devices with sophisticated designs. Moreover, the waveguide offers an efficient medium for nonlinear optical functions. In terms of advanced telecommunications, the silicon nano-wires are unsurpassed and provide many important implications for the improved manufacture of organic-based photonic wires. Their major limitation is the very small dimensions that do not facilitate largescale light collection.

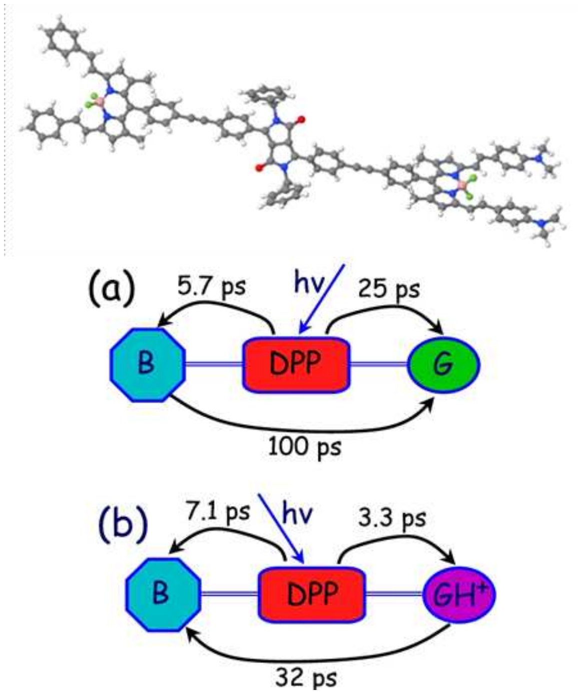

Figure 13. Illustration of the molecular triad developed for directed EET. (a) Illumination of the central diketopyrrolopyrrole (DPP) fragment leads to rapid EET to the expanded Bodipy terminal (B), folllowed by long-range EET to the opposite terminal G. (b) After selective protonation of bthe green dye, G, the direction of EET is reversed.

Scaffold-supported arrays for distributive EET

To prevent aggregation of the chromophores and to ensure their optimal positioning, photosynthetic light-harvesting arrays are built around protein scaffolds. Chromophores are attached via non-covalent interactions which, in certain cases, can selectively modulate the spectral properties. This is a wonderful display of precision engineering that operates effectively over large surface areas, as in green plants. Other subtleties are inherent to phototrophic bacteria and photo-active enzymes. In general, the role of the protein is to isolate the reagents from mutual electronic perturbations while maintaining high density and structural integrity. Such effects are difficult to duplicate with artificial materials but several interesting examples have described the use of a scaffold to assemble multi-chromophore arrays capable of intra-cluster EET. Additional examples use polynucleotides or helical proteins for much the same purpose.

Contemporary synthetic chemistry provides the tools by which to attach several disparate chromophores to a single platform.[56] The intention is to increase the dimensionality of the array and this situation is nicely illustrated by recent work[57] using triptycene as the supporting platform (Figure 14). Here, three disparate Bodipy dyes are covalently attached to the triptycene core in such a way that they retain their individual optical signatures but are sufficiently close to promote Förster-type EET around and across the rigid support. In fact, the rates of EET are fast (i.e., picosecond timescale with the EET probabilty for each step exceeding 90%) in this system, although the geometry might enable a modest range of orientations that display somewhat different EET characteristics. The terminal acceptor absorbs at around 610 nm and emits in the far-red region. Related systems have been built from truxene platforms[58] decorated with three different phosphorescent transition metal complexes. In this case, triplet energy transfer occurs between the Pt and Ru centres until the triplet exciton is trapped at an emissive Os centre. Other inert supports have been devised from such diverse materials as ZnO nanorods,[59] microporous polymer nanoparticles,[60] oligo-phenylethynyls,[61] macroscopic beads,[62] and designer peptides.[63]

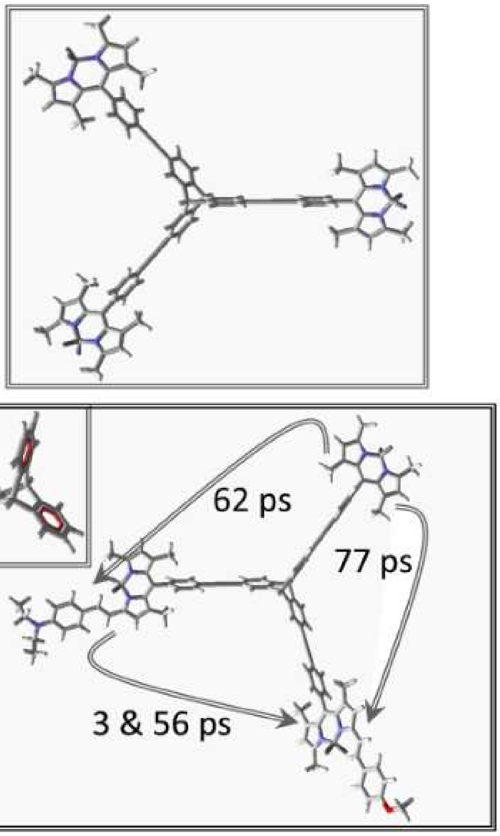

Figure 14. Molecular formula and EET pathways for the molecular triad comprising three disparate Bodipy dyes built around the triptycene platform (lower panel). The insert serves to illustrate the unique geometry of triptycene in terms of positioning the attached chromophores. Also shown is the complementary molecular triad bearing three idental Bodipy-based dyes (upper panel).

In the context of 3-dimensional supports, it is natural to give consideration to the fullerenes as spherical scaffolds, especially since recent synthetic modifications have led to the discovery of relatively soluble analogues.[64] Indeed, the hexaadduct of C_{60} lends itself to the synthesis of decorated supports bearing 12 dye molecules; in one such case,[65] the attached dyes correspond to 10 yellow Bodipy dyes and 2 blue Bodipy dyes. Selective illumination into the yellow dye is followed by fast EET to a nearby blue dye, but also to exciton migration to adjacent yellow dyes. In this manner, the exciton spreads around the sphere until trapped at one of the blue dyes. The overall trapping efficiency is 78% in fluid solution and 85% when the particles are dispersed in a plastic film. In the absence of the blue acceptor, exciton migration competes with fluorescence.

An unusual feature of this system[65] is that EET occurs between decorated particles, both via exciton migration among yellow dyes and through EET from yellow to blue dyes attached to different particles. This inter-particle exciton diffusion occurs in the solid state at high loading. Unfortunately, the transit time needed for the exciton to sample different particles is quite long (i.e., ca. 1 ns) relative to inherent decay of the yellow dye (i.e., ca. 5 ns) so that diffusion is likely limited to a single jump. Nonetheless, this is the closest artificial analogue of the natural light-harvesting complex yet reported and experiments have confirmed its ability to sensitise amorphous silicon solar cells.

Alternative types of supported EET arrays can be constructed from porous media able to accommodate emissive guests.[66] An obvious advantage of such materials is that they can be used in the solid state. Several approaches to this end have been reported, including zeolites,[67] hydrogen-bonded networks,[68] biological polymers,[69] layered double hydroxide nanosheets[70] and single crystals.[71] Precise positioning of the substrates is a problem, as is the actual dimensionality of the EET processes, but interesting models can be assembled this way without the need for covalent chemistry. It has not, as yet, been possible to devise next-generation artificial light-harvesters by this methodology.

Self assembly of artificial light-harvesting arrays

It was recognised in the early 1990s that constructing elaborate artificial photosynthetic systems based on covalent chemistry was extremely time consuming. Attention turned to the emerging field of supramolecular chemistry as a cost-effective way to assemble intricate multicomponent structures. Sessler,[72] in particular, pioneered the self assembly of porphyrin-based conjugates via multiple hydrogen bonding. Such entities were found[73] to display either (singlet and triplet) EET or light-induced electron transfer across the assemblage. Hydrogen bonding tends to be rather weak, however, and such structures lack the stability for practical applications. Alternative ways to build up layers of light-harvesting units include π,π stacking, electrostatic interactions and coordinative binding patterns.

There is, in fact, a long history of photoactive aggregates being formed by π,π stacking of flat chromophores, such as the cyanine dyes used in the early days of colour photography. At first sight, this situation seems to be at odds with the many reports stressing that aggregated dyes are nonfluorescent. However, the formation of H- or J-aggregates overcomes this particular problem and, in certain cases, can lead to strongly emissive particles. Similar behaviour is found for quantum dots where the photophysics can be tuned by controlling the dimensions of the particle. The main problem with such aggregates relates to their tendency to give rather narrow absorption spectral profiles. Nonetheless, there are clear indications that J-aggregates can function as effective sensitizers for certain semiconductors.[74]

Disc-like chromophores equipped with peripheral chains of inert hydrocarbons can be employed to create columns of π-stacked dye molecules. Such columns might incorporate several hundred chromophores in a regular array.[75] Despite the close proximity of the dye molecules, these columns often display discrete HOMO and LUMO levels and fluorescence characteristic of the array. As happens with many conjugated polymers, π-stacked dye molecules fall into small domains which can effectively localise the exciton, which tranverses the column. In fact, an incredibly diverse library of aggregated structures has been obtained with functionalised arylene imides and dimides and their close associates.[76] Many of these structures undergo highly efficient, rationale energy migration among the subunits within the emergent monodispersed aggregates. More remarkable has been the observation[77] that certain units self-associate into hydrogen-bonded, two-turn helices that grow to lengths of about a micron and form bundles of tubular structures in the solid state.

Recently, the concept of ionic self assembly was used to form liquid-crystalline materials based on two disparate Bodipy dyes (Figure 15).[78] In the liquid phase, the reactants associate to give a 2:1 complex in which EET is quantitative. This stable complex can be partially dissociated by addition of a competing ion so as to alter the efficiency of EET, probably because of an accompanying structural relaxation. Heating the solid film leads to evolution of a liquid-crystalline material, as characterised by X-ray diffraction, that also exhibits quantitative EET. Related studies have demonstrated the development of functionalised organo-gels that support EET processes between the constituents.[79] Such materials appear to be practical and suitable for large surface area applications but, at present, lack the necessary functionality.

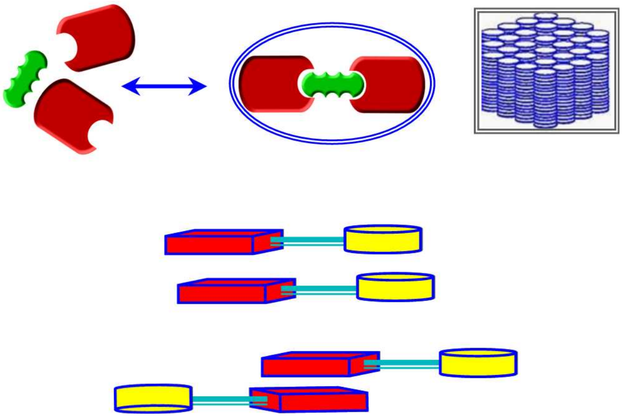

Figure 15. Cartoon style representation of the ionic self-association of disparate Bodipy-based building blocks into a tripartite molecule able to form a columnar liquid crystal upon heating. The lower features indicate self-association of the corresponding covalent dyad upon cooling (upper) and under high pressure (lower).

Metal complexes, most notably metalloporphrins, can be manipulated to provide an accessible coordination site with which to assemble complex structures. This subject, which was developed most notably by Sanders[80] and Sauvage[81] and their coworkers, allows the contruction of linear, cyclic, and tubular arrays of chromophores and provides easy access to triplet excited states. There are many examples of rapid EET within such networks. Extension of the basic concept leads to the templated formation of porphyrinic wheels whereby a porphyrin-based molecular ribbon wraps around the template in a cyclic fashion before the ends are joined.[82] The net result is a macrocycle containing multiple porphyrins, each linked to the central core. These materials bear a striking resemblance to the arrays found in the natural light-harvesting machinery and, in many cases, are capable of effecting efficient electronic energy migration around segments of the network.

New concepts

The conventional way by which to couple an artificial photon collector to a photochemical device (e.g., a solar cell) is to incorporate the former into a plastic film. With an appropriate polymer, such as poly(methylmethacrylate), fluorescence from the organic dyes is directed towards the edges of the film by way of total internal reflection. In this manner, it is possible to engineer films capable for directing up to 80% of absorbed photons to the edge of the film[83] and thereby to the device. A weakness of this approach is that the plastic sheets, which might be of considerable surface area, tend to be less than 1 cm thick. Improvements are possible in the form of specialised coatings that reflect light from the lower surface back into the bulk[84] and by matching refractive indices for film and device using thin optical layers.[85] The net gain is a vastly decreased surface area for the opto-electronic device and better control over photon management. Of course, a critical feature concerns the stability of the organic film over prolonged exposure to sunlight and considerable attention has been given to this point in terms of searching for more robust but relatively cheap plastics. Bear in mind that the polymer film, when exposed to strong sunlight, might attain temperatures in excess of 40 ^{0}C for many hours at a time. It should also be stressed that, despite being around for at least three decades,[86] these luminescent solar concentrators have not found widespread acceptance in the solar cell market. Improvements in both design and application are called for but there is the possibility to take advantage of new materials that are becoming available. One such material is a highly scattering form of paper[87] that could be impregnated with a fluorescent dye. Such systems could be highly valuable in terms of defocussing high intensity light fluxes and also in terms of ensuring that the device could be properly powered when kept away from direct illumination.

Recently, there has been a move towards replacing organic dyes with quantum dots and for involving plamonic excitation of metal particles. Such systems tend to be photostable but lack the versatility and easy handling of organic dyes. Hybrid systems, using a combination of a quantum dot and organic sensitizer, are much less developed but could hold promise for useful photon collectors. Rather surprisingly, there have been relatively few reports describing the use of conjugated polymers as solar concentrators,[88] perhaps because of design limitations. In all, not much engineering work has been devoted to fabricating new types of solar concentrator,[89] despite the availability of vastly improved dyes. While considerable advances have been made with fluorescent gels, rubbers, liquid crystals, paints and inks, such materials have rarely been used as light harvesting media.

Concluding remarks

Tremendous progress has been realised in terms of the design and synthesis of elaborate molecular architectures capable of highly effective cascade-type EET. Such arrays are able to collect almost all incident sunlight above a particular threshold frequency and direct the excitation energy to a preferred fluorophore. These arrays, although challenging in terms of synthesis, can be expected to show vastly improved light-harvesting performance when compared to a cocktail[90] of the same dyes unattached by covalent or supramolecular connections. The most notable gains are in terms of improved stability and reduced self absorption. These are serious problems for conventional luminescent solar concentrators (LSC) that can be overcome with well-designed multi-component arrays. Improved stability is achieved because the excited-state lifetimes of individual chromophores are too short for photodegradation to compete with EET along the cascade. With the correct shape (Figure 4), damaged chromophores can be by-passed and the only unit susceptible to real damage is the terminal acceptor. The large cluster-type arrays are less prone to aggregation because of their complex three-dimensional arrangements while self-absorption is prevented by both concentration (as in the V-shaped structures) factors and careful choice of the terminal acceptor.

The nature of the terminal acceptor now determines the overall performance of the array. There is a risk that the products formed by photodegradation of this unit catalyse destruction of the chromophores higher up the cascade process. Clearly, this has to be addressed via engineering protocols. It does, however, open up the possibility for introducing some kind of self-repair mechanisms. As yet, such processes are not available. Instability of the final acceptor diminishes if the exciton can be off-loaded rapidly and irreversibly to the photochemical device. This situation is not easily achieved in artificial prototypes but is inherent to natural light-harvesting complexes. We have no artificial analogue of the FMO complex to link the photon collector to the charge accumulator. This has to be the next phase of development.

In fact,the probability for retaining fluorescence within the light-harvesting unit, assuming this to be a plastic film, can be pushed to increasingly high level by surface treatment and plasmonic effects.[91] New materials, such as highly scattering media,[87] can be utilised to ensure that most of the absorbed photons reach the photochemical device. Such strategies do not overcome problems of exciton annihilation, rather they encourage this loss mechanism, and opportunities exist for the design of new approaches for integrating light collection and photochemistry. The natural photosynthetic machinery positions the charge accumulator within the photon collector and this seems to be the best direction for putative artificial prototypes.

Notes and references

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†As a crude generalisation, the two main EET mechanisms involve through-space (TS) and through-bond (TB) interactions. The TS process does not require the reactants to lie within orbital contact but involves an orientational dependence that stems from coulombic terms. The rate of TS EET increases with decreasing separation distance (usually displaying the well-known R^{-6} dependence) and depends critically on the spectral overlap integral. The donor must be emissive. In contrast, the TB process

demands orbital contact, often by way of super-exchange interactions imposed by a conjugated bridge, and closely resembles Marcus electron transfer. This mechanism holds for triplet excited states and is usually operative at short separations. The donor does not have to be a good emitter.

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Table of Contents Entry

Following natures' blueprint, the concept of artificial light-harvesting antennae is discussed in terms of sophisticated molecular arrays displaying a tailored cascade of electronic energy transfer steps.