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Bio-Inspired Artificial Light-Harvesting Arrays Based on Boron(III)-Chelates

Hatun H.T. Al-Sharif and Anthony Harriman

Abstract

Many diverse natural systems use sunlight to drive critical chemical reactions. To harvest sufficient photon densities, natural organisms have developed highly sophisticated light absorbing antennae rather than rely on direct illumination of a single chromophore. Attempts to develop artificial analogues have resulted in the synthesis and spectroscopic characterisation of elaborate molecular assemblies and here we consider the case for using boron(III) chelates as the primary light absorbers. Such entities make attractive modules for the creation of multi-component arrays with individual units sited in a logical sequence for long-range electronic energy transfer. Alternatively, certain boron(III) chelates can be synthesised in high yield by simple strategies that avoid time-consuming purification. These latter materials are appealing as components for large-scale light harvesters. The use of photonic crystals avoids the need to position individual molecules at the catalyst but presents severe design challenges. Interrupting, or redirecting, the flow of excitons within the array requires the introduction of novel switches that can be activated by selective illumination. Protecting the array against adventitious photofading is a major objective that has yet to be achieved.

Keywords: fluorescence, electronic energy transfer, photophysics, chromophores, covalent networks, photonic crystals, photosynthesis

1. Introduction

Most chemical reactions that occur in biology have to be performed under mild conditions. With few exceptions, this means running the reaction at atmospheric pressure and temperatures at around 37°C. The main solvent is water. Despite such severe restrictions, Nature is able to supply an inordinately wide variety of chemicals on an enormous scale. Extensive use is made of enzyme catalysts, templates and protein matrices to assemble the required materials and to ensure selectivity. A further challenge inherent for much of natural synthesis is the need to produce chiral products with high specificity. During evolution, Nature has learned to re-use a basic molecular structure for multiple purposes simply by making minor, but critical, changes. The other key trick used by Nature is to arrange a limited number of building blocks in different sequences so as to engineer unique structures comprising only a handful of simple modules. The most illustrious examples of this particular strategy are the polynucleotides.

By way of slow evolution, Nature has learned many other tricks. One that is relevant here concerns the attachment of light-harvesting proteins to catalytic sites so as to achieve high rates of photochemical synthesis. Photochemistry is surely the cleanest, simplest and most effective means for driving high-energy reactions. Such processes invariably require a catalyst to perform bond making, or maybe bond breaking, steps. These enzymes are optimised for the difficult thermal chemistry, which might involve multi-electron steps, and usually lack the chromophores needed to absorb sunlight at a reasonable level. The answer to this conundrum is to append a light harvester to the enzyme with the sole purpose of channelling absorbed photons to the active site. This approach is employed throughout all biological processes that use light to initiate a chemical reaction. The light harvester ranges from a single molecule, as found in photolyase DNA repair enzymes, to the intricate molecular machinery developed for photosynthetic bacteria and plants. These latter systems involve several hundreds of individual chromophores arranged cooperatively to collect photons of disparate frequency and direct the exciton to the correct location.

Although the structure and function of many natural light-harvesting systems has been reviewed in detail, much remains to be learned about the assembly process. Some photon collectors are self-repairing and contain built-in redundancy to compensate for inevitable damage during operation. This is the case for the Fenna-Matthews-Olson complex found in photosynthetic bacteria [1]. The natural systems are often equipped with ancillary protective mechanisms. For example, light-harvesting membranes contain high levels of carotenoids [2] to protect against accidental generation of oxy-radicals and singlet molecular oxygen. The other critical issue to emerge from a study of the natural units is the realisation of the staggering amount of material involved. We can illustrate this point by considering the following features of the biological world:

- Wheatgrass contains up to 70% by mass of chlorophyll, the main pigment of natural photosynthesis;
- Green plants contain several different types of chlorophyll, each possessing a different absorption spectrum to maximise overall light collection;
- Photosynthetic bacteria contain roughly 200–250 molecules of chlorophyll for each catalytic site responsible for fuel production;
- Reliable methods for measuring chlorophyll content indicate levels ranging from 41 mg m^{-2} up to 675 mg m^{-2} according to geographical location and type of organism;
- The 45-acre site at Clayhill in Bedfordshire, one of the UK's operational solar farms, generates enough power for 2500 homes. Assuming 50% of the acreage is taken up with solar panels, this would be the equivalent of at least 10 kg of chlorophyll;
- The current cost of BODIPY (see below) is £170 per gram and a typical synthesis might produce 2 g of purified material.

The main conclusion drawn from this crude analysis is that protocols for the efficient synthesis of the dye are as important as the optical properties. Indeed, it is essential that high yields of compounds for artificial light-harvesting applications

are attainable under conditions that do not require elaborate, or time-consuming, purification procedures. The basic operating principle for an artificial light-harvesting array is sketched in **Figure 1**. Individual chromophores are arranged in such a way that each compound can absorb a fraction of incident sunlight. To provide for panchromatic absorption, a minimum of three separate chromophores is required while each absorber needs to be equipped with ancillary chromophores to broaden the spectral response. The resultant exciton can be transferred around the network until reaching the terminal acceptor where it can be off-loaded to the device. The latter removes the exciton from the array so as to fulfil some useful task.

We now enquire about the possibility of constructing simple artificial light-harvesting systems using tetrahedral boron(III) chelates as the generic building block. These chromophores are based on small repeat units in which the boron atom plays the critical role of assembling the unit into a macrocyclic structure with extended π -conjugation running along the molecular backbone. A variety of such units is available. Each unit can be equipped with secondary features to aid solubility or modulate physiochemical properties. Units can be linked together to create new electronic entities with synergistic performance. Chirality can be introduced by several different means, if required. Below is given a generic model to better illustrate the design features (**Figure 2**). One such molecule acting alone is never going to solve the light-harvesting problems and so it is necessary to import some means for selective accretion of molecules into patterned arrays. At a rough guess, it might be necessary to equip each catalyst with 100 or more chromophores to ensure a high photon flux reaching the reactive site. This realisation adds further complexity to the final design, which has to go much further than simply identifying some useful building blocks. It is clear, even at the beginning of our search, that the individual units must be cheap, stable, safe-to-handle and easily recycled. A further requirement is the need to develop a repair strategy but this might be too advanced for the moment! We begin by considering likely boron(III) chelated modules.

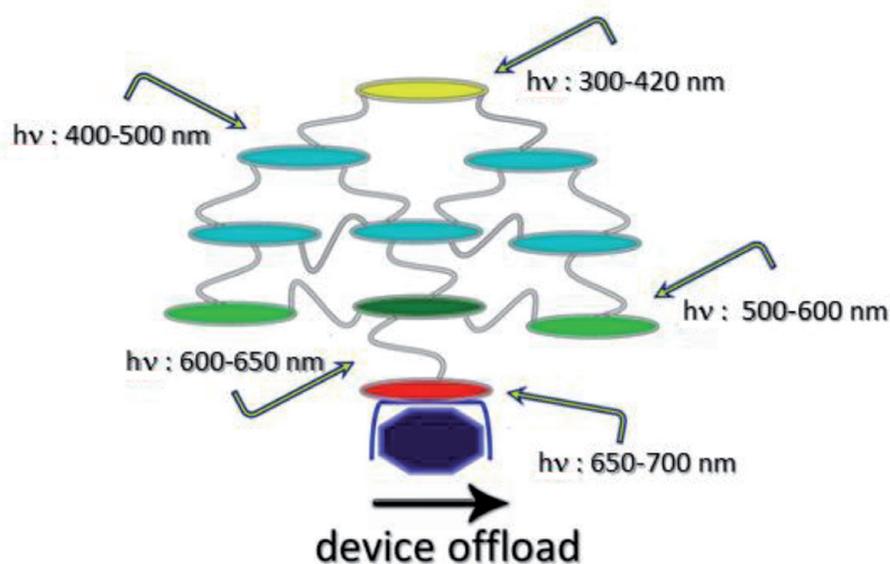


Figure 1.

Pictorial representation of a putative artificial light-harvesting antenna. Each disc is intended to represent a boron(III) chelate equipped with ancillary chromophores. Each of these discs is designed to collect photons over a particular wavelength range. Electronic energy transfer can occur between the various discs; this will be reversible for identical chromophores but will be irreversible when there is an energy gradient. The final boron(III) chelate (coloured red on the scheme) is closely associated with a device, which removes the photon from the array. Individual EET steps must be fast to avoid photofading of the chromophores. The varied routes available to EET reflect the need for redundancy.

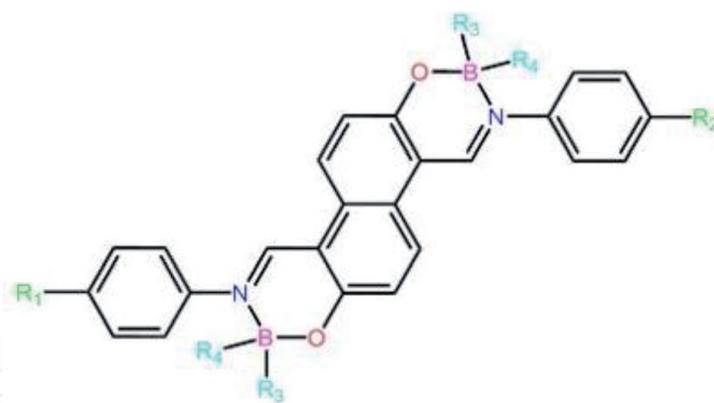


Figure 2.

Illustration of the functionalisation of the basic boron(III) chelate used as principle light absorber. The various sites indicated by the symbol “R” can be used to improve physicochemical properties, such as solubility, and to tune the optical properties. This level of derivatisation is necessary for identifying optimum photonic crystals.

2. Boron dipyrromethene (BODIPY) chromophores

Without doubt, the family of boron dipyrromethene (BODIPY) [3, 4] dyes has inherited the title of “Queen of Fluorophores” over the past decade or so. The basic structural framework facilitates almost limitless opportunities for modification and expansion, leading to a bewildering variety of compounds. The conventional structure, shown in **Figure 3**, has a planar geometry around the dipyrryn unit imposed by the tetrahedral boron(III) site. In general, two types of “conventional” BODIPY dyes are distinguishable according to the provision, or not, of an unconstrained *meso*-aryl ring. Steric clashes between adjacent hydrogen atoms restrict rotation of

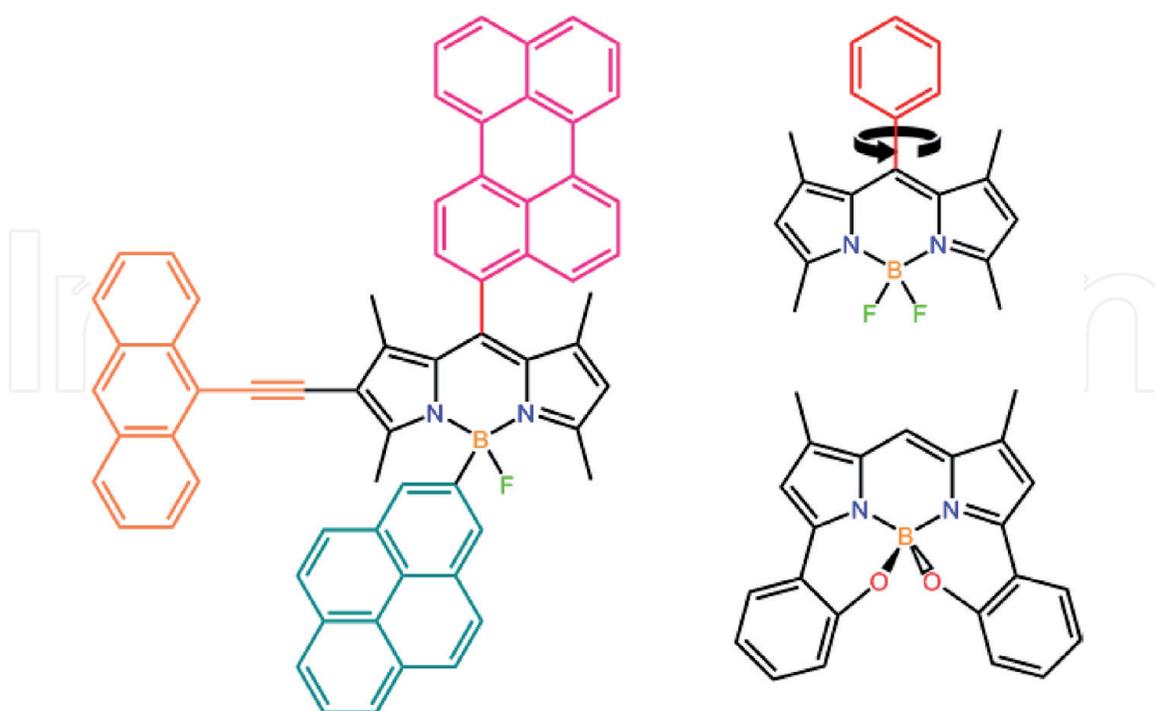


Figure 3.

The upper right-hand panel represent a conventional BODIPY dye equipped with a rigidifying BF_2 residue. Substituents can replace the hydrogen atoms at any of the carbon atoms while it is possible to exchange one or both fluorine groups with a wide variety of organic residues. The *meso*-site, otherwise known as the 8-position, is especially interesting in as much as aryl hydrocarbons can be attached and used as energy donors. The lower right-hand side shows a chiral derivative. The left-hand panel shows how the basic BODIPY nucleus can be equipped with ancillary light harvesters so as to provide for panchromatic photon collection.

this aryl ring around the connecting C-C bond and this leads to modest distortion of the dipyrin backbone. The result is an interesting class of fluorophores known [5] as “molecular rotors” that can be used to report on rheology changes. These compounds tend not to be strongly fluorescent and are of limited value in terms of photon concentrators. The other type of conventional BODIPY fluorophore uses alkyl groups to block gyration of any *meso*-aryl ring and the resultant compounds tend to be highly emissive under all conditions. It is a simple matter to disperse these chromophores in plastic sheets to give highly effective luminescent solar concentrators, where a high fraction of the fluorescence appears at the edges of the film. Suitable attachment to a solar panel provides the means to sensitise the semiconductor towards particular segments of the solar spectrum. Such devices have particular relevance to organic solar cells.

These classical BODIPY dyes are robust, easily functionalised, photochemically stable and strongly fluorescent. Typical absorption and fluorescence spectral maxima lie in the 470–550 region. Fluorescence quantum yields tend towards unity while excited-state lifetimes are typically around 5 ns. Lindsey et al. reported the first example of the incorporation of such BODIPY dyes into artificial light-harvesting systems in 1994 [6, 7]. Their system used a terminal BODIPY dye to inject excitons into a linear array of porphyrinic chromophores (**Figure 4**). Electronic energy migration and transfer results in long-range transport of the exciton from the BODIPY dye to the distal terminal, supplemented by secondary light absorption by the zinc porphyrins. This system was the starting point for an avalanche of related arrays capable of vectorial exciton migration. The main design principle for these systems is to create a gradient of excitation energies that facilitates stepwise transfer of the exciton along a molecular-scale wire.

Since the original report, a wealth of such artificial arrays has appeared in the literature, synthesised by many different research groups. The common goal is to use a series of disparate chromophores to absorb different regions of the solar spectrum and transfer the excitation energy along a linear or branched chain. A certain fraction of the energy is lost at each stage but, by careful positioning of the reagents, very fast (i.e., sub-ns) electronic energy transfer can be engineered. By judicious choice of chromophore, energy transfer can be unidirectional and almost quantitative [7]. The exciton ultimately reaches a terminal site where it needs to be off-loaded to some kind of device, such as a solar cell or light-active catalyst (**Figure 1**). Some of these arrays possess elaborate three-dimensional structures that can collect considerable numbers of photons over a wavelength range spanning many hundreds of nanometres. One of the largest such architectures is depicted in **Figure 5** and contains a total of 21 chromophores packed into a small volume. An added attraction of these artificial arrays is that the individual energy transfer steps can be monitored by time-resolved optical spectroscopy.

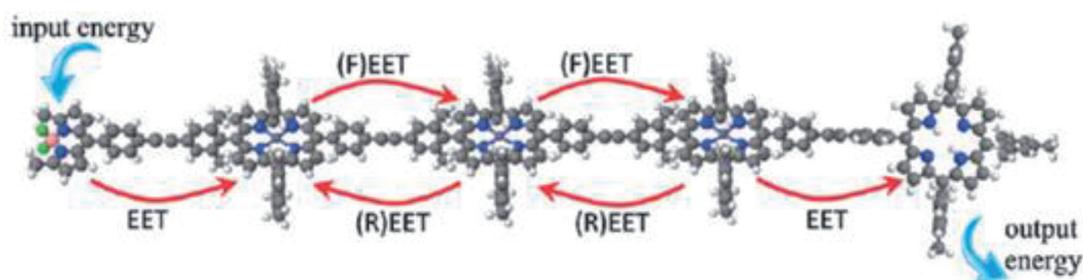


Figure 4. Prototypic molecular-scale wire, comprising a BODIPY-based dye as input unit, three zinc porphyrins capable of forward and reverse energy transfer and a terminal free-base porphyrin as the emitting output unit. Reproduced from Ref. [7].

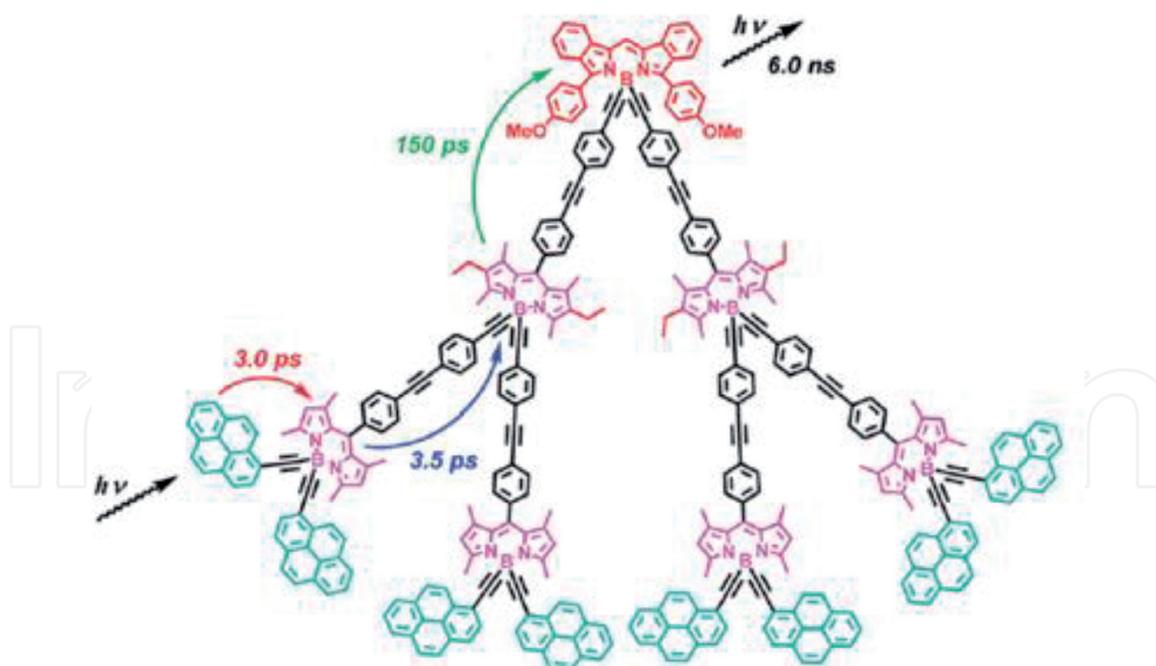


Figure 5.

Molecular formula for the large artificial light-harvesting array comprising 21 discrete chromophores, with the lifetimes indicated for each of the main units. Reproduced from Ref. [7].

It will not have escaped attention that these artificial light-harvesting arrays require quite sophisticated synthesis, involving multiple steps with low overall yields. They are expensive to produce and it seems unlikely that large quantities could be prepared by robotic methods. The latter is essential to generate sufficient quantities of material for practical application. Fortunately, the arrays seem to be relatively photostable. This is because the excited-state lifetimes of the dyes that contribute to the energy-transfer cascade are kept very short and also because the BODIPY nucleus does not favour intersystem crossing to the triplet manifold with reasonable efficacy. Only the terminal dye is susceptible to photobleaching and only if the deactivation of this unit is slow – for example, when the device is inoperable. This situation has been described by Stachelek et al. using a multi-component BODIPY-based array [8] (**Figure 6**). Here, the molecule undergoes stepwise photobleaching leading to successive loss of individual chromophores but retains photoactivity at all stages. The net result is that the array can absorb more than 10 million photons and still remain operational. Nonetheless, the protracted synthesis appears to rule out such systems as being viable for largescale artificial light-harvesters.

Lindsey et al. have questioned [9] if such arrays are effective as photon collectors. Their approach has involved detailed consideration of the required density of chromophores at a planar semi-conductor surface needed to effect a useful level of sensitization. This density has to take into account the absorptivity of the chromophore, its molecular volume, surface coverage and ancillary chromophores able to transfer excitation energy to the ultimate donor. Their general conclusion is not too encouraging for the practical application of covalently linked chromophoric arrays. This realisation has led the Lindsey Group to look at bio-hybrid systems whereby artificial pigments replace natural analogues in protein-based matrices. The intention is to make use of the protein to achieve very high chromophore densities having the minimum wastage of molecular volume.

Other research groups have sought alternatives to the covalent synthesis needed to assemble molecular architectures such as that shown in **Figure 4**. For example, supramolecular systems can be built by intercalating suitable chromophores into DNA. This avoids the need to link together the individual reagents via covalent

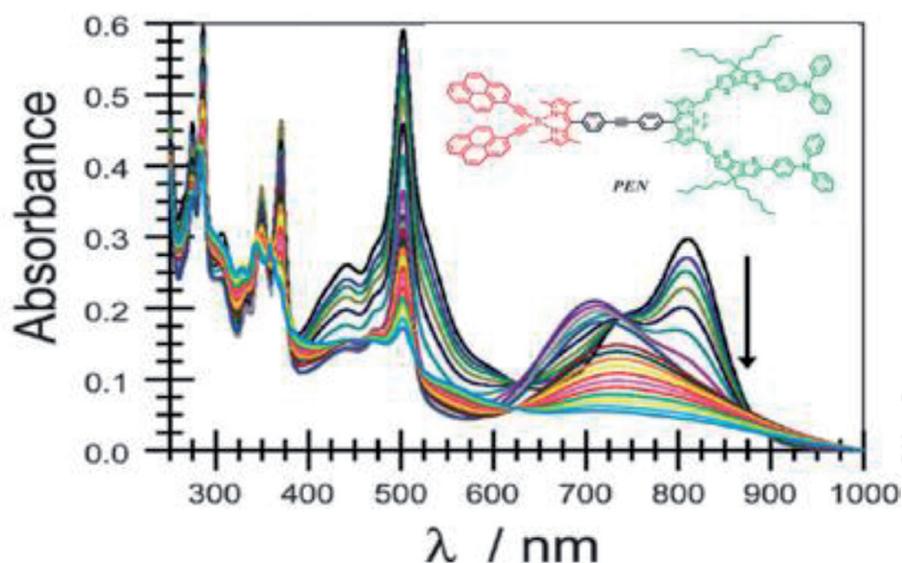


Figure 6. Effect of continuous illumination with white light on the absorption spectrum recorded for PEN in deaerated CH_2Cl_2 . Spectra were recorded at regular intervals over a period of 100 hours. Reproduced from Ref. [8].

synthesis but it becomes more challenging to position the reagents in a logical sequence. Other approaches to the same end include accretion of individual chromophores into aggregates that retain photoactivity. Such assemblies might be stacked columns of planar dyes or J-aggregates. Their main advantage is that many hundreds of chromophores can be self-assembled into one giant structure, driven simply by solvophobic effects. A further benefit of this approach is that the columns can be easily dismantled and re-assembled in the event that an individual component becomes damaged during operation. This kind of replacement would be difficult, if not impossible, for the elaborate covalent networks.

3. Symmetrical pyrrole- BF_2 (BOPHY) modules

Over the past few years or so, the supremacy of BODIPY as a fluorescent reagent has been challenged by a series of new fluorophores, one of which is termed BOPHY [10] (**Figure 7**). This latter compound is easily synthesised in high yield and provides for formation of a wide variety of derivatives. It is not as versatile as BODIPY but is a very useful building block for preparation of linear molecules. Despite its longer π -conjugation pathway, the lowest-energy absorption maximum observed for BOPHY is blue shifted relative to that of BODIPY and is more complex. Unlike

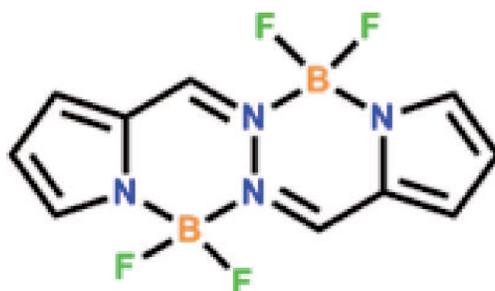


Figure 7. The molecular formula for the basic BOPHY core, where different substituents can be appended at the various carbon atoms. Also shown is a solution of BOPHY in CHCl_3 solution with and without UV illumination. The final panel illustrates a fluorescent chemical sensor developed for the detection of copper(II) cations in fluid solution.

BODIPY, there is poor mirror symmetry between absorption and fluorescence spectral profiles, at least in the liquid phase [11]. However, the lowest-energy absorption transition is broadened relative to BODIPY and this is a useful feature for a putative photon collector. Recently, BOPHY has been used as the emissive segment of certain types of fluorescent sensor. The tetrahedral geometry around the BF_2 groups helps to minimise self-association and BOPHY-based compounds tend to be highly soluble in common organic solvents. Other studies have shown that bromination of BOPHY results in a compound able to sensitise formation of singlet molecular oxygen under illumination in fluid solution. Additional work has described the photochemical bleaching of BOPHY in liquid and solid phases. It appears that the compound is highly resistant to photofading under visible light illumination [12].

Ziessel et al. have reported [13] on the properties of the first molecular dyad built around the BOPHY scaffold (**Figure 8**). Here, a perylene moiety has been linked to the BOPHY core by way of an ethynylene group, thereby ensuring both close proximity and strong π -conjugation. These authors reported that direct excitation into the perylene group causes rapid electronic energy transfer to the BOPHY unit. The latter emits at long wavelength because of the increased conjugation. This raises the question as to whether exciton passage from perylene to BOPHY is internal conversion or intramolecular electronic energy transfer. Other fused ring BOPHY derivatives have appeared very recently where the main absorption transition can be tuned across the visible spectral range. These materials are useful building blocks for creation of multi-component light-harvesting arrays but such molecular assemblies have not yet been reported.

Related research has considered ways to design redox-active BOPHY derivatives [14]. The basic BOPHY framework is equipped with styryl units that extend the π -conjugation pathway in a linear fashion. The styryl units are terminated with N,N-dimethylamino groups that can be protonated or oxidised. This simple strategy allows the evaluation of long-range electronic interactions between the terminal groups as the charge increases. It might be stressed that adding conjugated groups to the BOPHY core is not too demanding in terms of synthesis and characterisation. However, there remains the problem of scale and questions about how best to produce large quantities of such material.

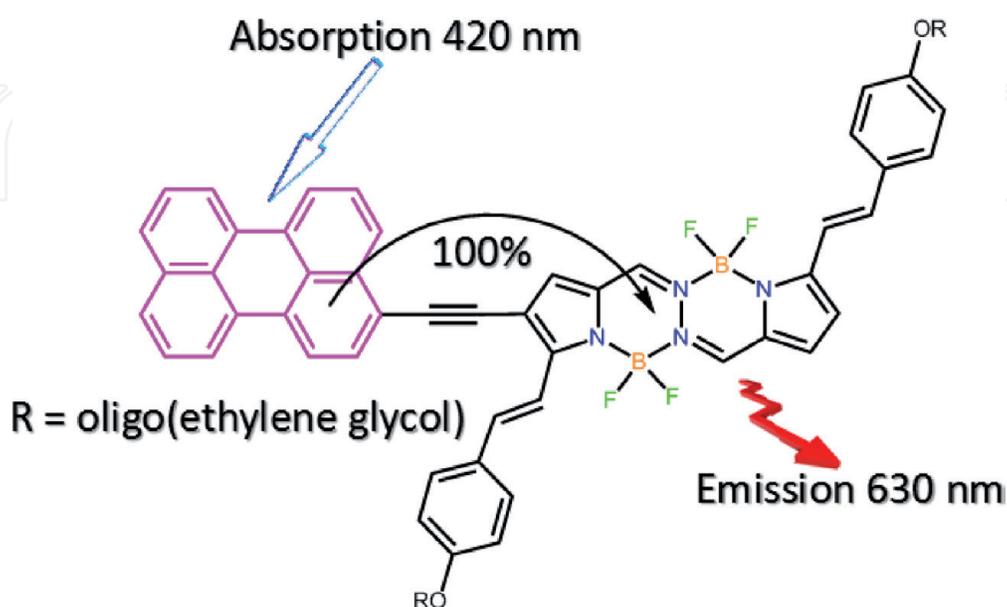


Figure 8.

Example of an artificial light-harvesting analogue constructed around the BOPHY chromophore. The light collection facility is expanded by adding a perylene function to the BOPHY unit. Excitons generated at the aryl hydrocarbon are transferred rapidly to the BOPHY unit, which itself emits at long wavelength.

One of the key features of the BOPHY family relates to its high fluorescence yield in the absence of perturbing groups. Fluorescence is almost quantitative for the simpler derivatives and BOPHY-based dyes are ideal candidates for inclusion within plastic luminescent solar concentrators. The S_0 - S_1 absorption transition is primarily HOMO-LUMO in nature and the radiative rate constant is high. Triplet state formation is negligible for simple BOPHY derivatives in solution but certain substituents are able to promote intersystem crossing. A report has appeared that describes emission from certain crystals formed from thiophene-substituted BOPHY [15]. It is anticipated that many more functionalised BOPHY derivatives will appear in the near future.

4. Related boron(III)-chelated chromophores

Four-coordinate organo-boron complexes have emerged as promising materials for optoelectronics, such as organic light-emitting diodes (OLEDs) and organic field-effect transistors. This work is still at the exploratory stage but the new boron(III) chelates offer real prospects for the development of a range of blue emitters. This is a wavelength range where there are relatively few efficient fluorophores having the necessary stability and electroluminescence performance. This is especially true for deep blue emitters, in marked contrast to the numerous red and green emitters that are already in the marketplace. Since, in general, certain boranils and boron β -diketonates are known to exhibit high fluorescence quantum yields in the solid state, together with good levels of photostability, these materials are beginning to attract attention. Examples of such compounds include the *mono*-boranils shown below in **Figure 9**.

Ziessel, in particular, has conducted a detailed search for alternative fluorescent dyes to the popular BODIPY family [16]. Both the type of ligand and the nature of the assembling boron(III) fragment has been considered. This has led to several classes of tetrahedral boron(III) compounds as illustrated via **Figure 10**. The range of available compounds can be extended by considering five-membered rings with quinolines or six-membered rings with salicylaldehydes, oxazolylphenolates, acylpyrrole, or pyridinephenolates. Additional six-membered rings have been formed from chelation to phenalene-1,3-dione and perylene diimides. Many of these novel systems are easily adapted to form binuclear complexes, such as those prepared around naphthyl ligands (**Figure 11**). In all of these cases, the synthetic strategy used to isolate the compounds is straightforward and avoids the use of complicated procedures. Quite pure materials emerge from the crude reaction mixtures without the need for protracted column chromatography. Unfortunately,

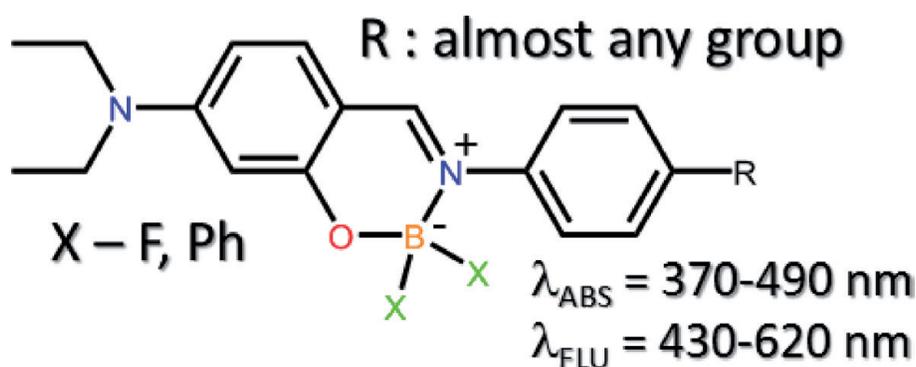


Figure 9. Molecular formula for the most common type of *mono*-boranil complexes built around the N-B-O pattern. The terminal R group can be varied to include many different functionalities.

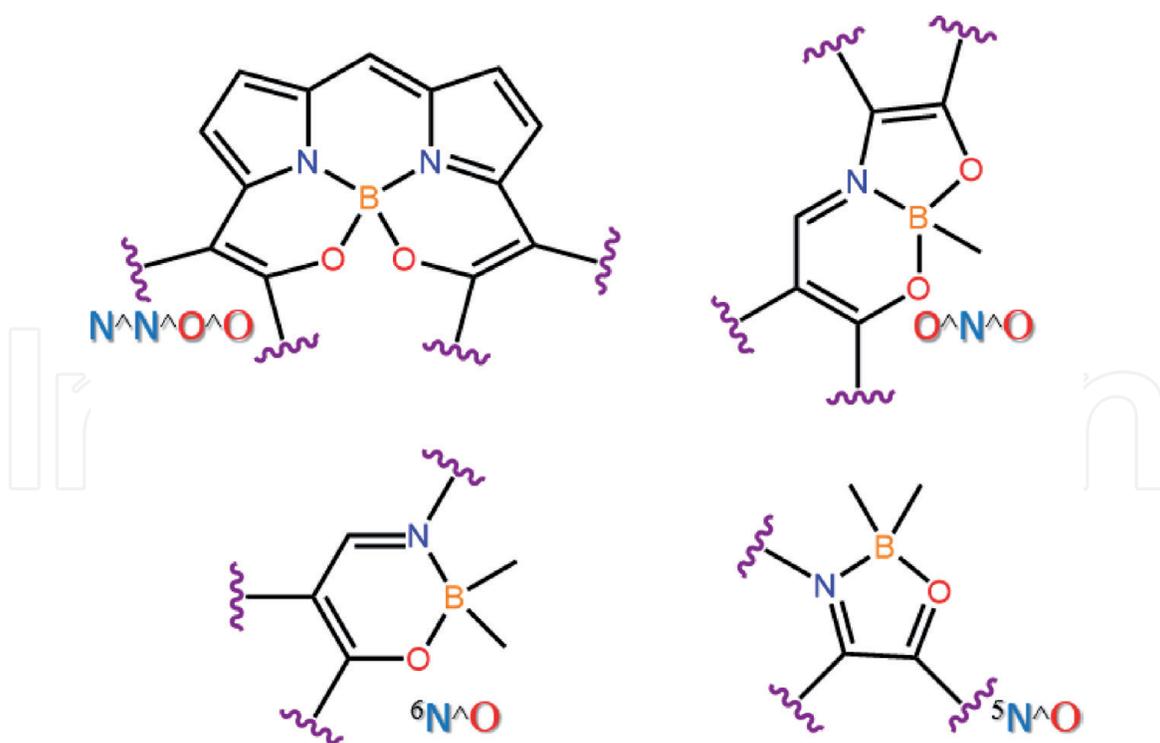


Figure 10.
Common type of chelating modes available to B(III) modules, as identified by Ziessel et al. [16].

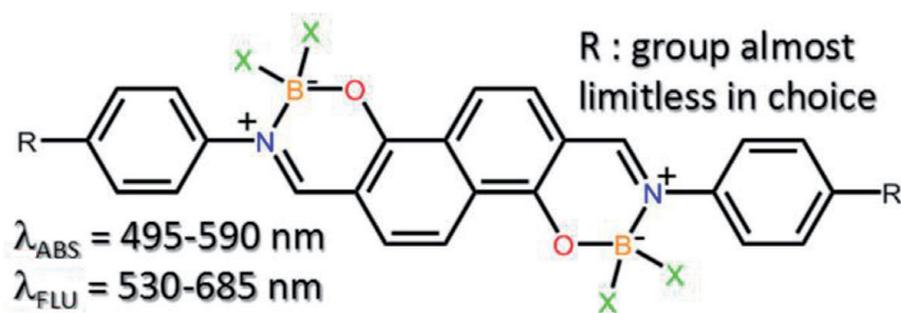


Figure 11.
Simple illustration of the construction of bis-boranyl complexes around the rigid naphthyl central core. The nature of the terminal group can be varied at will while different functional groups can be attached to the boron(III) sites. The absorption and emission spectral properties can be modulated over a wide range.

the fluorescence quantum yields tend to be low, at least in solution, and thereby restrict the application of the compounds as solar concentrators. This is not the case for the rigid naphthyl-bridged binuclear complexes shown in **Figure 11** where emission quantum yields can approach 90% [17]. One added advantage of these simple chelates is the ability to synthesise optically resolved fluorophores in good yield. These latter compounds are rare among the boron(III) chelates in as much as their absorption and emission maxima, molar absorption coefficients and quantum yields are independent of the nature of the solvent.

5. Functional arrays

Returning momentarily to **Figure 1**, it can be seen that the array has a built-in element of redundancy to cover for damage to any particular chromophore. Even so, the terminal acceptor plays an important role and must be protected against damage. It must also fit tightly to the device in order for irreversible electronic energy transfer to be quantitative. The question raised by Lindsey et al. [9] concerns

the ability of the array to deliver sufficient numbers of photons per unit time for the system to operate effectively. The device could be an organic solar cell or a molecular catalyst engineered for fuel production. In this latter case, the gap between arrival times of successive photons is crucial since the formation of stable chemical products requires multiple electrons. In order to avoid the damaging effects of free radicals, it is essential that charge accumulation is completed before the intermediate radical can escape and cause damage. In the case of a solar cell, the performance requires excitation with the optimum flux of photons. A single light-harvesting array of the type depicted in **Figure 1** is incapable of supplying the necessary input. The solution is to design systems where many individual arrays combine to furnish the device with sufficient photons. Since it is unlikely that a large number of arrays can be packed around the device in a logical manner, it follows that systems have to be designed whereby fast electronic energy transfer between arrays occurs with very high efficiency. Only one such system has been reported to-date [18] but the rate of energy transfer was too slow for practical operation (**Figure 12**). New design strategies are needed if progress is to be made in this critical direction.

A second concern about the viability of artificial light-harvesting antennae is the inevitability of chemical damage during prolonged exposure to sunlight. It seems impossible to completely prevent loss of chromophores during operation and, at present, we have no successful strategies for in-situ repair of damaged components. Approaches need to be found, therefore, to by-pass damaged units without compromising the overall antenna. This might be achieved using dyes that can be selectively protonated so as to induce a large change in the absorption spectrum when exposed to acidic conditions. There will be a significant alteration of the corresponding spectral overlap integral for electronic energy transfer and this simple modification will allow the direction of exciton migration to be controlled. This behaviour is illustrated by way of **Figure 13**, where the molecular antenna presented as **Figure 1** is re-examined.



Figure 12.

Pictorial representation of artificial light-harvesting array built by attaching disparate BOBIPY derivatives to a functionalized C60 residue. At high concentration in a thin plastic film, electronic energy migration proceeds between adjacent particles decorated with the yellow dye and exciton trapping occurs at the blue dye. This is a rare example of long-range energy transfer between particles. Reprinted with permission from [18]. Copyright (2012) American Chemical Society.

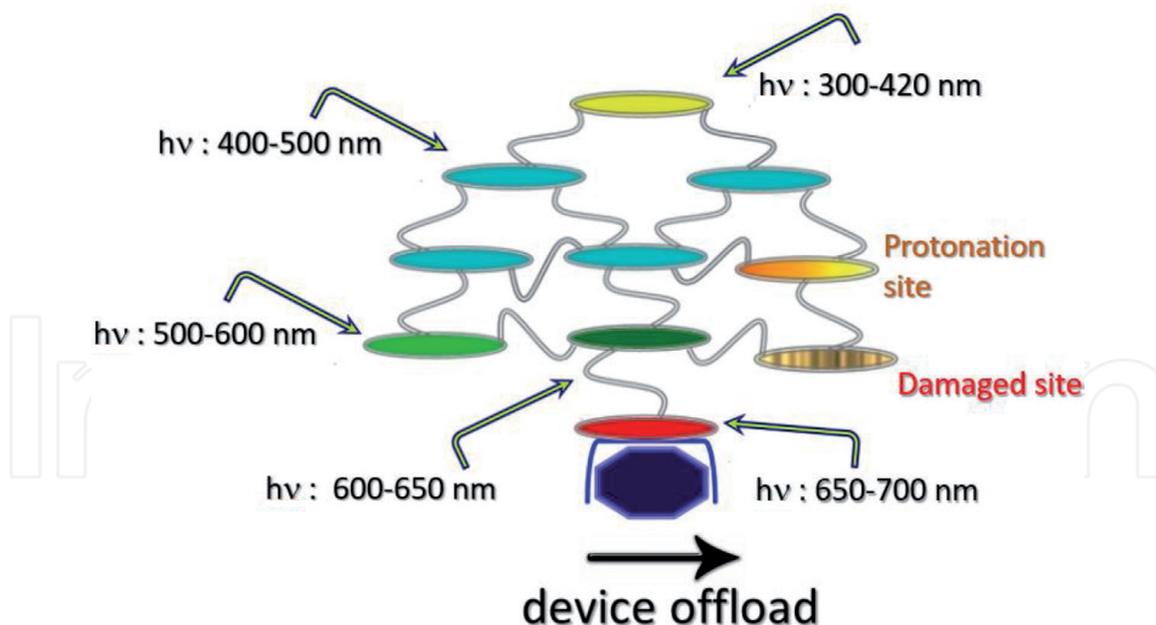


Figure 13.

Modification of the generic set-up indicated in **Figure 1** to include the likelihood that one of the components will become damaged during prolonged exposure to sunlight. Such damage leads to release of a proton, which becomes attached to an adjacent chromophore and changes the absorption spectral profile. This in turn switches-off electronic energy transfer to the damaged site and re-directs the exciton within the antenna.

It is presumed that under continuous illumination one of the components will become damaged. There are growing indications that such photofading of the chromophore follows autocatalytic kinetics, meaning that the system appears stable for a considerable period but suddenly starts to bleach. The product could catalyse further damage by, for example, formation of long-lived triplet states. Bleaching is often accompanied by release of a proton and this could be collected by an adjacent chromophore. Provided protonation leads to a marked change in colour, electronic energy transfer along that segment of the antenna could be interrupted and excitons directed elsewhere within the system. This leads to self-protection without loss of performance and avoids excitation of damaged components that might otherwise activate radical formation. **Figure 14** shows an example of a molecular triad that fulfils the desired objective [19]. Protonation can also be effected using a photo-acid activated with near-UV light.

One of the most important lessons learned from examination of the natural light-harvesting array is that, in all likelihood, successful artificial analogues will need to possess the facility to transfer excitons over hundreds of identical

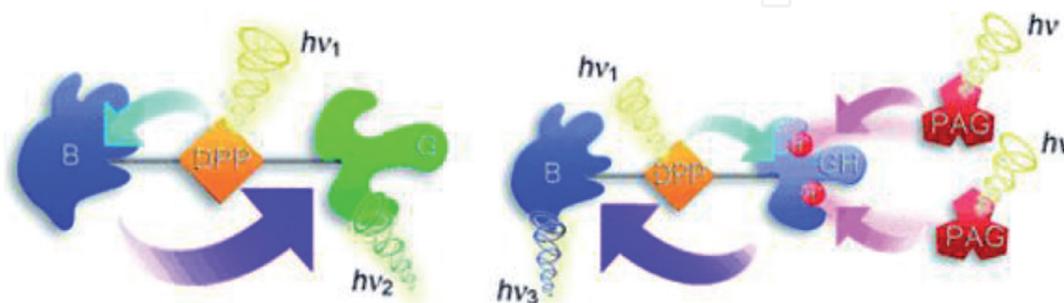


Figure 14.

Illustration of the use of a photo-acid to alter the direction of electronic energy transfer in a molecular triad. For the neutral molecule, photons absorbed by the central dipyrropyrole (DPP) unit are transferred rapidly to the green BODIPY terminal. This latter unit is protonated on illumination of a photo-acid generator (PAG). This changes the optical properties of the dye and, as a consequence, EET now occurs to the blue BODIPY dye. Reproduced with permission from [19].

chromophores. The direction of energy transfer cannot be controlled under such conditions because there is no driving force. Energy transfer will resemble a random walk. To be efficient, individual chromophores will need to be closely spaced but not so close that π,π interactions provide a route for fluorescence quenching. These realisations have led us to consider the use of photonic crystals as the basis for our artificial light harvesters. This might appear a rather bizarre strategy because it is well known that fluorescence quenching is usually very effective for high fluorophore concentrations in fluid solution due to self-association. There is the additional problem of self-absorption, which also tends to curtail fluorescence. None-the-less, crystals offer several key advantages relative to plastic films, most notably the very high absorbance that can be achieved. There are now several reports describing fluorescence from boron(III) chelates under visible light illumination.

Early work in this field noted that single crystals assembled from a BODIPY derivative equipped with a *meso*-tetrathiophene residue were fluorescent [20]. Selective excitation of the oligothiophene unit at 400 nm was followed by fast electronic energy transfer to populate the fluorescent state of the BODIPY dye. Such observations are important because they indicate close packing of the molecules in the crystal lattice does not necessarily restrict the photophysical properties of the molecular dyad. In other work, it was reported that BODIPY derivatives fitted with aryl groups in place of the conventional fluorine atoms formed crystals that were significantly more fluorescent than the same compound dissolved in fluid solution [21]. The crystal hinders rotation of the B-aryl groups and this closes down an important radiationless pathway. This is a further example of what is currently termed “aggregation-induced emission”. The same crystals assemble into “columns” with adjacent units being co-facial, having a centre-to-centre distance of ca. 9.0 Å, but slightly offset and with the boron atoms lying on the same side of the molecule. Such arrangements could facilitate electronic energy migration along the column in a random walk (**Figure 15**).

Photonic crystals based on BODIPY derivatives contain an amorphous region in addition to the ordered columns. These somewhat disordered regions appear to facilitate dimerization, or higher-order aggregation, of the chromophore which is evident as a red-shifted absorption band. These self-associated species can operate as traps for excitons migrating along the ordered columns. This long-wavelength

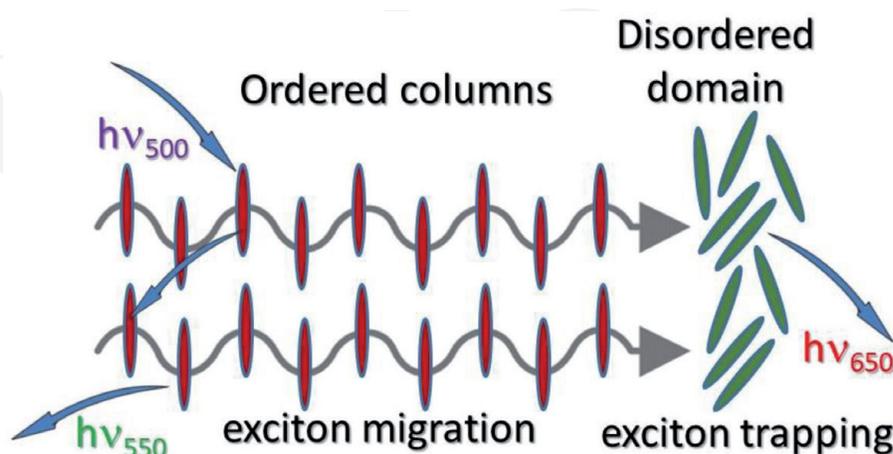


Figure 15.

Schematic representation of the photophysics that follow illumination of a BODIPY chromophore within the crystal lattice. The arrangement of molecules into layers provides an ideal environment for rapid electronic energy transfer along the layer. This process competes effectively with fluorescence such that an exciton might sample several hundred individual dye molecules. The exciton can hop between columns on a slower timescale. Aggregates form in a more amorphous region and, because of a red-shifted absorption spectrum, these act as traps for excitons migrating along the layers. It is quite rare for aggregates to fluoresce. Reproduced with permission from [21].

emission is in addition to the usual Frenkel-type fluorescence so that the overall fluorescence profile is broadened considerably. The same is true for the absorption spectrum. Our studies indicate that the aggregates can possess quite long-lived excited states and are therefore possible candidates as energy donors for opto-electronic devices. Constructing such systems represents the next phase of this project.

This work might pave the way for new types of artificial photon concentrators possessing high densities of chromophore. It is necessary to identify crystals where π,π -interactions are at a minimum and this could mean introducing steric blocking groups to keep individual molecules at some preferred distance. New experimental techniques will be needed to monitor the photophysical properties of single crystals, probably making use of fluorescent microscopes. However, by working closely with crystallographers, it should be possible to compile a set of rules regarding the best criteria for isolating photonic crystals suited for fast electronic energy transfer followed by strong fluorescence from a defect state. Such materials have many advantages compared to intricate covalent architectures.

6. Conclusion

In several respects, boron(III) chelates can be considered ideal candidates for building photonic arrays where many chromophores act cooperatively to harvest sunlight and to subsequently drive a useful device. The tetrahedral geometry around the boron atom favours the design of multi-component structures where the subunits are not in strong electronic communication. The same structural feature helps to isolate individual chromophores in the crystal lattice, despite the close proximity of neighbouring molecules. The basic macrocycle assembled around the boron(III) centre can be modified, expanded, diversified and functionalized with almost no limit, so as to provide access to an enormous range of compounds. Most of these materials are emissive, although it is necessary to avoid systems that are based on intramolecular charge-transfer processes. Fluorescence is often retained in the solid state and this is an unusual feature that can be well exploited to develop artificial photon concentrators.

This latter field has produced some wondrous examples of accreted molecular entities capable of highly efficacious electronic energy transfer within the cluster. The next stage of development requires groups of such clusters to operate together so as to amplify the number of photons concentrated at the device in unit time. This is a major challenge that demands the introduction of new types of synthetic methodologies. In principle, photonic crystals can solve this particular problem and can be doped at the surface with fluorescent traps. However, there remains the need to attach the crystal to the device without loss of performance of either unit. The field is only now beginning to fulfil its promise and it is likely that operational photonic crystals will soon emerge.

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Conflict of interest

The authors declare no conflict of interest.

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Author details

Hatun H.T. Al-Sharif and Anthony Harriman*
Molecular Photonics Laboratory, Newcastle University, Newcastle upon Tyne,
United Kingdom

*Address all correspondence to: anthony.harriman@ncl.ac.uk

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