
STUDY ON COST EFFECTIVE METAL AND METAL FREE DYES

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ABSTRACT

After the discovery of the DSSC in 1991, researchers and businesses working in this industry worked toward the goal of commercialising this category of solar devices by finding materials that were efficient (the former) and stable (the latter). However, after approximately 30 years and taking into consideration the "energy issue" that is now facing society, the durability of the materials that are being used cannot be regarded a pointless spine of the efficiency DSSC. Considering that there is no Holy Grail recipe, future research in this field can and should be driven by green metrics and LCA. From here on out, these three ideas ought to proceed hand in hand with one another. "Stable," "Effective," and "Sustainable" ought to be the adjectives associated with forthcoming innovative materials and processes. Carbon dioxide is a greenhouse gas that has recently emerged as a significant risk to the health of our planet's ecosystem. It is important to note that, as was touched on briefly in the paragraphs that came before this one, the efforts that have been made toward developing more environmentally friendly materials have been more focused on individual components (such as the sensitizer, redox couple, electrolyte, and counter-electrode) rather than full devices

KEYWORDS : *Cost, Metal, Dyes*

INTRODUCTION

The Sun is technically a flow resource rather than a renewable energy source since it is a continuous supply of electromagnetic radiation that is unable to replenish itself. This means that the Sun cannot be stocked with energy. The Sun, on the other hand, is an example of a source of renewable energy since, at least in the context of human history, its energy is infinitely replenishable. Because their rate of extraction is lower than their rate of consumption, energy derived from renewable resources can be considered a workable starting point toward the development of truly sustainable sources (this is especially true in comparison to the sources of energy generated by fossil fuels). The production of sustainable energy does not always need the use of renewable resources, as is obvious. In point of fact, this goal can only be accomplished through the use of effective technology, in which the manufacturing and dissemination of said technology is not hindered by the availability of resources.

In light of this, newly developed photovoltaic (PV) technology, and more specifically dye-sensitized solar cells (DSSCs), have the potential to improve energy efficiency and the proportion of energy that is generated from renewable sources by virtue of the specific applications that have been listed above. These technologies are designed to work in conjunction with conventional solar panels.

DSSCs are photo electrochemical devices that were initially co-invented by O'Regan and Gratzel. These devices are considered to be a part of the group of developing PV technologies. They have been researched and developed for more than twenty years as a credible alternative to the well-established p–n junction photovoltaic devices made from silicon. This is due to the rapid and simple preparation methodology they use, along with their environmentally friendly and sustainable production. Nowadays, with the strong advent of newly developed perovskite solar cells (PSCs), the lead-based thin-film technology that has quickly and significantly outclassed the record PV efficiencies by a factor of two on both rigid and flexible configurations, promising to compete with silicon technology in the near future, the effective role and prospects of DSSCs for utility-scale solar applications have been overshadowed. This is because PSCs have quickly and significantly overclassed the record PV efficiencies by a factor of two. However, as of right now, there are only a limited number of perovskite materials to choose from, and the issues of their stability and toxicity continue to be extremely challenging; as a result, DSSCs and other emerging photovoltaic technologies must be considered still viable, and they can be developed, perhaps simultaneously, for many years into the future. This will provide the opportunity to design solar cells with a great deal of flexibility in terms of shape, colour, and transparency. In comparison to technologies based on silicon, direct semiconductor solar cells (DSSCs) have a lower efficiency and a shorter life-time, which are the two primary obstacles to the broad commercialization of DSSCs. However, despite the significant drop in the cost of silicon, DSSCs continue to provide a significant benefit in that they are able to maintain their functionality even when exposed to diffuse light. In addition to this, they are capable of being constructed as see-through devices, which enables them to serve as intelligent, power-generating building blocks.

In point of fact, DSSCs still represent a competitive alternative technology, particularly in contexts where low production costs and environmental benignity are primary requirements. This is the case for three primary reasons: (i) their simple preparation methods can contribute to exploiting solar energy in a sustainable way, increasing its use, and promoting climate change mitigation; (ii) the opportunity to produce devices that do not contain any critical raw materials; and (iii) their foreseen exploitation. On the other hand, DSSCs

Nevertheless, in spite of these benefits, the commercialization of DSSC requires a great deal more work. As a result, a significant amount of research is focused on the development and optimization of each of the components of DSSC in order to increase their lifetime and efficiency while simultaneously reducing costs and negative effects on the environment. Accordingly, numerous in-depth and informative articles have been published over the course of the past ten years, which reviewed the advancements and challenges in the field of DSSCs. These articles ranged from S. Anandan's analysis of the various components of DSSCs and the effect of nanostructuring in 2007, to K. Sharma et al.'s review of the fundamentals and current status of the field, as well as the general trends and developments in the field of photoelectrodes, While Shalini et al. gave an in-depth discussion on the various types of sensitizers, J. Wu et al. concentrated their efforts primarily on the counter electrode (CE) component of the devices, which included metals and alloys, carbons, and conductive polymers. Shalini et al.'s study was published in Science. D. Sengupta and colleagues provided new insights into the critical function of the photoanode as well as the influence of influencing factors on the photovoltaic properties of the device. On the other hand, some writers have focused their attention on the characteristics and composition of the electrolyte in order to achieve the optimal balance between efficiency and stability.

OBJECTIVE:

1. To study the artificial photosynthesis in a variety of chromophores.

2. To study on the concept of sustainability applied to dsscs

THE CONCEPT OF SUSTAINABILITY APPLIED TO DSSCS

A great number of articles and book chapters on DSSCs have been published in the literature, as was mentioned in the introduction. In these publications, leading scientists working in this field have extensively reviewed the working principles, architectures, chemistry, physics, materials science, engineering, and smart technology behind DSSCs. It has been investigated whether the use of new materials can improve the effectiveness and reliability of DSSCs. However, these new materials can be prohibitively expensive, hazardous, environmentally unfriendly, and/or produced through labor-intensive and resource-intensive processes that make it challenging to mass-produce them at prices that are competitive with existing options. In point of fact, the expense of reaching the maximum possible device efficiency outweighs the real goal behind inventing a certain category of solar cell technology. This technology needs to be kind to the environment while also being cost-effective in terms of its manufacture. In point of fact, over the course of the past few years, a growing amount of emphasis has been placed on ensuring the longevity and ecological friendliness of the newly manufactured gadget components.

It is important to keep in mind that just because a machine generates energy from a renewable source does not automatically make it sustainable. In point of fact, the production of energy from renewable sources comes with its own set of problems and challenges, such as the incorporation of CRMs into the relevant technological processes. ⁸⁹ As a result, it is of the utmost significance to conduct research into the primary variables that are responsible for posing a danger to the long-term viability of a certain technology in order to develop a form of renewable energy that can in fact be described as sustainable.

The life cycle assessment (LCA) is a powerful instrument that can be used to investigate the environmental sustainability of a product or service. This method permits the evaluation of the product's impacts on the environment as well as the identification of the primary contributors, also known as "hotspots." The findings of an LCA are defined by several levels of uncertainty, where the lower the uncertainty level, the more thoroughly the life cycle of a product is analysed. When it comes to DSSCs, the large-scale manufacturing phase and the end-of-life (EoL) phase are not yet mature. Because of this, the accuracy of the results that have been provided can be enhanced in the future when there will be more data available and the processes will be more defined. In addition, a large number of LCAs for DSSCs have been investigated using the "cradle-to-gate" methodology. This method examines the whole life cycle of DSSCs, beginning with the extraction of raw materials and ending with the production phase (the use phase and the EoL are not considered due to the lack of data for waste management). Following that, the LCAs that are published in the literature deal with "established architecture," which makes use of typical materials that are known for their high levels of performance. As a result, the vast majority of the innovative materials that have been presented throughout this review have not been investigated by means of an efficient LCA. Nevertheless, if LCA data are available, we have critically analysed the preparation procedures of a specific material in paragraphs that are dedicated to that material. On the other hand, in cases when LCA data are not readily available, we identified potential "hotspots" that will be taken into account in a next evaluation.

The cumulative energy demand (CED) and the energy payback time are also additional indications that should be taken into consideration for PV energy systems (EPBT). The term "CED" refers to a type of energy indicator that calculates the total amount of energy demanded by a product across its entire life cycle. It is derived by

adding up the direct energy contributions (such as the electricity used in production and the thermal energy), as well as the indirect energy contributions (such as the embodied energy of the materials). It is possible to think of EPBT as a quantitative evaluation of the cost-effectiveness of a certain technology since it is an indication that is represented in years and represents the amount of time needed to create the same quantity of energy that is spent during the manufacturing operations (and its constituent materials). According to the following equation, the EPBT is dependent not only on the CED but also on the yearly energy output (YEO) and the electrical conversion factor (C). $EPBT = CED \cdot YEO^{-1} \cdot C^{-1}$. When discussions of novel materials take place in the scientific literature, CED and, more generally speaking, EPBT are two characteristics that are frequently ignored. Throughout the entirety of this review, we attempt to conduct a qualitative analysis (since the actual numbers are not available in the literature) of the synthesis and deposition procedures of materials that have been characterised as sustainable (or, more generally, cost-effective). Our goal is to provide evidence of the primary factor(s) that can have a negative impact on both parameters.

In addition, while doing an analysis that is motivated by sustainability, one cannot only analyse the consequences on the environment; rather, one must also take into account the socio-economic variables. In the European framework, commodities that are designated as CRM should be replaced, and their recovery should have priority. These materials are defined by supply risk and economic relevance.

Dye-sensitized solar cell

Even though it is already on the market, the dye-sensitized solar cell, also known as the DSSC, is one of the emergent alternatives that is considered to be one of the most developed technologies. This method, in contrast to the others, employs the utilisation of a liquid electrolyte; although, all-solid and quasi-solid states have also been produced. The record for cell efficiency presently stands at 12.6 percent. When contrasted with crystalline silicon cells or any number of other up-and-coming technologies, DSSC displays a lower efficiency. Long-term stability and electrolyte leakage are two more areas that provide difficulties. On the other hand, DSSC has advantages such as simple and inexpensive production techniques, high efficiency even under conditions of diffuse and low light intensities, colourful end products and flexible substrates, and advantages for the integration of buildings. The fundamental mechanism behind DSSC light harvesting is the absorption of light by molecules of dyes that are tethered to the surface of a semiconductor mesoporous layer. In most cases, nano particles of TiO₂ are used for this purpose. These dyes are commonly made of synthetic materials that are rare and toxic and are based on ruthenium (Ru), but they can be replaced by plant pigments, which are friendly to the environment, inexpensive, easily extracted, and widely available, despite the fact that they do not have the same level of efficiency and stability as the synthetic dyes. DSSCs that are created using natural dyes are frequently referred to as natural dye-sensitized solar cells (NDSSC).

Although the majority of published studies are still below this range, Iqbal et al. brought numerous published works displaying NDSSC efficiencies between 1% and 2% to the attention of their 2019 review audience. In a remarkable achievement, Sanjay and colleagues were able to generate cells using *A. amantacea* and *P. pterocarpum* leaves that had an efficiency of 8.22 percent when grown in ethanol.

DYE-SENSITIZED SOLAR CELLS: STATE OF ART AND FUTURE CHALLENGES

The fundamental concept of photosynthesis, which takes place within the mitochondria of plant cells, was the original motivation behind the development of DSSCs. The concept of artificial photosynthesis has been around

for many years, but to this day, it has not been successfully implemented in an industrial setting to generate renewable energy. This is due to the fact that artificial photosynthesis is a complicated multi-step process that needs to be optimised, which frequently requires materials that are both expensive and hazardous. Because it imitates the way in which natural processes absorb energy from sunlight, DSSC photovoltaic technology may be compared to an artificial kind of photosynthesis.

PHOTOSENSITIZERS FOR DSSCS

Because it is responsible for the primary function of collecting photons from sunlight, giving electrons to the semiconductor, and then turning the sunlight into electrical energy, the photosensitizer, also known as the dye, is one of the most essential components of DSSCs.

In order for a dye to be regarded an effective PS for DSSCs, it is necessary for the dye to meet many important conditions, which are as follows:

134 I a high molar extinction coefficient with panchromatic light absorption ability (from the visible (VIS) to the near-infrared (NIR) region); (ii) the ability to strongly bind to the semiconductor through an anchoring group (typically, a carboxylic or hydroxyl group), so that electrons can be efficiently injected into the semiconductor CB; (iii) the ability to absorb light in a wide range of wavelengths; (iv) the (iii) a good highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energy alignment with respect to the redox couple and the CB level in the semiconductor, which allows efficient charge injection into the semiconductor, as well as simultaneously efficient regeneration of the oxidised dye; (iv) the electron transfer rate from the dye sensitizer to the semiconductor must be faster than the decay rate of the PS; and (v) stability under solar light illumination. Therefore, the particular function of sensitizers as well as the method by which they operate is intimately connected with both the photoelectrode and the redox mediator. In point of fact, the design of an efficient PS ought not to ignore the reciprocal interactions that take place between both of these components. The adsorption of the PS onto the photoelectrode should lead to the highest surface coverage (to limit the back-transfer reaction between electrons in the CB of the semiconductor and the redox mediator) without giving rise to multilayered structures, which promote the self-quenching of the excited state. This is because the back-transfer reaction between electrons in the CB of the semiconductor and the redox mediator can be limited. On the other hand, the LUMO of the sensitizer should be delocalized as close as possible to the anchoring site in order to promote effective charge injection into the semiconductor CB. On the other hand, the HOMO should be delocalized in the portion of the molecule that is facing the electrolyte in order to promote the regeneration process. This is because the HOMO is responsible for promoting effective charge injection into the semiconductor CB. We consider three primary kinds of dyes among the most effective sensitizers. These include functionalized oligopyridine metal complexes, Zn-based dyes (Zn-porphyrins and Zn-phthalocyanines), and completely organic dyes. Functionalized oligopyridine metal complexes are the most effective. The most significant problems associated with the majority of these PSs include I the potential release of hazardous chemicals as by-products, (ii) the utilisation of toxic reagents/catalysts, and (iii) the quantity of organic solvents that are required for the synthesis and purification steps of these PSs. Furthermore, in the case of metal-based molecules, where rare metals such as ruthenium and osmium are used, the primary concern is the use of CRMs. This makes the overall production of the device highly dependent on rare resources, which makes it non-sustainable and uneconomical from the perspective of large-scale production.

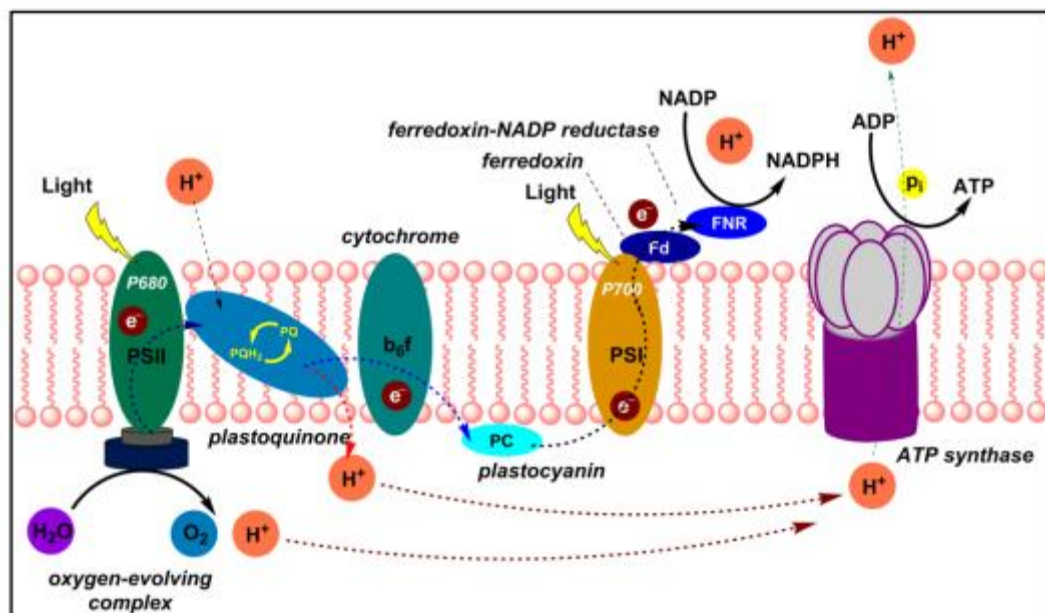
The high amount of solvents and eluents that are consumed during the synthesis of the dye is the primary factor that contributes to its negative impact on the environment. However, different LCA results indicate that the dye only accounts for a very small portion of the overall impact (less than 3 percent). Because the dye loading capacity of a DSSC is generally approximately 3×10^{-7} mol cm⁻², the quantity of dye that is required for the sensitization of a semiconductor is quite restricted. This implies that in the case of N719 and a squaraine dye, 0.35 or 0.20 mg cm⁻² are required, respectively. According to the calculation shown here, it is evident that the PS is not responsible for the total impact, in terms of expenses, that the entire device has, and as a result, the urgency with which its replacement with a solution that is more environmentally friendly is reduced. In spite of this, the metal centre is the most influential component when thinking about colours based on ruthenium. It is noteworthy to note that while evaluating the affects of YD2-o-C8, D5, and N719 (Zn-porphyrin dye, organic metal-free dye, and Ru-based dye, respectively), the latter has the least influence due to the fact that its synthesis has been effectively optimised. This finding was made. The optimization of the synthesis of Ru-based dyes is also obvious from the relatively low prices at which these dyes are available on the market in comparison to organic dyes. For instance, the price of N719 is just 65 euros per gramme, but a squaraine-based dye costs 400 euros per gramme.

In addition, it is important to note that ruthenium-based dyes have been the subject of extensive research and have been shown to have some of the best PV properties, with conversion efficiencies that are higher than 11 percent. Since these dyes have already been exhaustively reviewed in the literature, we will not be looking into their role any further in this article.

However, in recent times, in order to overcome the limitations of the use of sensitizers that are based on rare metal complexes, the scientific community has focused on replacing them with other PSs that have comparable efficiencies. These other PSs are going to be briefly discussed in the following paragraphs. On the other hand, removing key ingredients is not the only criterion that must be satisfied in order to accomplish the goal of producing a dye that is more environmentally friendly. For this reason, it is essential to combine life cycle assessment (LCA) with green metrics in order to analyse the entire consequences on the environment.

NATURAL PHOTOSYNTHESIS

Figure 1.3 depicts the sequence of events that take place in green plants, algae, and cyanobacteria during the natural process of photosynthesis, which plays an important part in the biological system. During this process, the energy of light is converted into the energy of chemicals through a series of events that take place in green plants. At the beginning, in the first step, the H₂O molecule is oxidised into O₂, and four electrons are produced. When these four electrons are put to use in the second phase of the process, the following reduction of CO₂ results in the production of energetic hydrocarbons, biomolecules, and carbohydrates.



Using cutting-edge X-ray crystallographic methods, the structure of membrane proteins that play a role in the process of photosynthesis was deciphered. The crystal structure of the photosystem II (PS II) found in thermophilic cyanobacteria was the first to be solved using this method. These studies offered information that helped to understand the mechanical features of charge separation (CS) processes, as well as catalytic events.

ARTIFICIAL PHOTOSYNTHESIS

The act of converting sunlight into a variety of various types of energy, such as chemical energy, electrical energy, and fuels, is known as artificial photosynthesis. This method involves imitating the natural process of photosynthesis. A typical artificial photosynthetic system is made up of a number of antenna units, each of which is made up of a number of different chromophores. These chromophores are able to effectively capture and absorb photons across the entire solar spectrum, and then channel that energy to the reaction centre (RC). The RC is the location where the photoinduced electron transfer (PET) and the efficient electron transfer (ET) from a donor to an acceptor both take place. It is also the location where the CS states are produced. The following components are required to be present in artificial molecular systems in order to achieve the steady conditions necessary to mimic the natural process of photosynthesis:

LIGHT-HARVESTING ANTENNA SYSTEMS

The light-harvesting systems consist of an assembly of photoactive molecules known as chromophores. These chromophores have been shown to have high absorption coefficient values in the visible and ultraviolet spectrums. These devices are able to gather light energy, which is then sent to the RC. Because no single chromophore is capable of absorbing all of the sun energy, a combination of chromophores with a wide range of electrochemical and optical characteristics is used instead. 15,16 On the other hand, these compounds should be able to be synthesised using simple synthetic processes and should contain favourable redox characteristics for efficient solar energy harvesting. This is because solar energy harvesting is a process that requires a lot of sunlight. As a consequence, due of the beneficial redox characteristics they possess, they need to be stable in both the ground state and the excited state. In a similar fashion, molecular linkers are used in the arrangement

of chromophores and for connecting the chromophores with energy reservoir. This is done in order for the molecular linkers to be able to allow for effective and rapid ET through the electronic blend without affecting the photophysical properties of each individual chromophore. The chromophores of the antenna are designed to take in the light energy, direct it to the RC, and then convert it into electronic energy. This is the ultimate purpose of the antenna.

REACTION CENTER

The energy trap and the D-A systems that are either covalently or noncovalently coupled to one other make up the reaction centre. The light energy that was captured was sent via the chromophores in D-A systems to stimulate electron transfer (ET), which produced charge-separated states by creating cation radicals on the donor and anion radicals on the acceptor. The RC is responsible for the transformation of electrical energy into redox energy. In the process of artificial photosynthesis, an efficient photosynthetic model must include light harvesting systems. Additionally, the reductant catalyst (RC) must be coupled with either a water oxidation catalyst or a CO₂ reduction catalyst that is capable of engaging in multielectron transfer processes. Following photoexcitation of the photosynthetic model, a multielectron transfer will take place, which will result in the transformation of raw materials with a low energy content (such as H₂O and CO₂) into raw materials with a high energy content (i.e., H₂, CO₂ reduced form). The oxidation of water results in the production of four electrons, while the reduction of protons needs two electrons. Redox energy is utilised in the production of chemical energy by the multielectron catalysts.

PHOTOINDUCED ENERGY TRANSFER

The capturing and absorption of photons is the essential step that must be taken in both natural and artificial photosynthesis in order to achieve superior photochemical conversion. The photons that are taken in during the process of photosynthesis serve as both the catalyst that starts and the driver of the entire photochemical conversion process. Therefore, in order to attain high quantum efficiency with little energy loss, a photo-induced energy transfer (PEnT) technique that is both efficient and reliable is necessary.

The process of the excitation energy being transferred from the chromophores to the RC is what is referred to as PEnT. In most donor-acceptor systems, the chromophores that capture light gather the photons and pump them into an energy reservoir. Subsequently, the energy that has been separated is used to build electrochemical potentials by ET cascades in the RC.

The chromophores in the antenna system are connected to one another by highly conjugated linkers. These linkers improve the electron coupling between the chromophores, which in turn helps to speed up the EnT process. Some EnT models, displaying effective EnT processes while having varied chromophore arrangements, are depicted in Figure 1.5. Figure 5a depicts the chromophore linear arrangement model, in which the chromophores are placed in a linear pattern and the EnT process takes place along a large number of paths to the RC. As a consequence, the potential for the greatest amount of energy loss exists within this model. The two-dimensional planar model is seen in Figure 7b. In contrast to the earlier model, this model requires a significantly lower total number of routes.

FORSTER ENERGY TRANSFER

Fluorescence resonance energy transfer, or FRET for short, is a mechanism that does not use radiation. It is also known as Forster Energy Transfer. During this process, the excitation energy from the excited donor molecule is transferred to the acceptor, which ultimately leads to the production of the excited acceptor molecule. In this mechanism, energy is transferred between two chromophores either by dipole-dipole contact or coupling (columbic interaction).

CONCLUSION

As potential new sources of renewable energy devices, DSSCs have garnered a lot of interest because to their low cost, simple manufacture, and high efficiency of energy conversion. An effort has been made to use natural dyes and aqueous electrolytes in order to replace the costly and hazardous components that are often found in DSSCs with ones that are less detrimental to the environment. Poor wettability, desorption of dye, low-diffusion coefficient of ions, recombination of photoanodes, and negative shift of the conduction band all contributed to the decreased efficiency of DSSCs based on natural dyes and aqueous electrolytes compared to conventional DSSCs. The performance of aqueous DSSCs has been enhanced as a result of a number of different initiatives, including the mixture of the dyes, the inclusion of the surfactants, and the treatment of the photoanode. Even though the efficiency of DSSCs is still somewhat low, a few experiments on entirely environmentally friendly DSSCs have been reported in recent years. Another important goal is to make the environmentally friendly DSSCs as stable as possible over the long term. It has been stated that an aqueous electrolyte might be more long-lasting than an organic solvent-based electrolyte. This could be because water has a low volatility, high surface tension, a high specific heat, and a high boiling point.

REFERENCES

- (1) Badgurjar, D.; Sudhakar, K.; Jain, K.; Kalantri, V.; Venkatesh, Y.; Duvva, N.; Prasanthkumar, S.; Sharma, A. K.; Bangal, P. R.; Chitta, R. *The Journal of Physical Chemistry C* 2016, 120, 16305.
- (2) Arrigo, A.; La Ganga, G.; Nastasi, F.; Serroni, S.; Santoro, A.; Santoni, M.-P.; Galletta, M.; Campagna, S.; Puntoriero, F. *Comptes Rendus Chimie* 2017, 20, 209.
- (3) Mirkovic, T.; Scholes, G. D. In *Photobiology*; Springer: 2015, p 231.
- (4) Mirkovic, T.; Ostroumov, E. E.; Anna, J. M.; Van Grondelle, R.; Scholes, G. D. *Chemical Reviews* 2017, 117, 249.
- (5) Forster, T. *Ann. Phys. Leipzig*. 1948, 2, 55.
- (6) Albinsson, B.; Mårtensson, J. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 2008, 9, 138.
- (7) Sahoo, H. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 2011, 12, 20.
- (8) Ma, L.; Yang, F.; Zheng, J. *Journal of molecular structure* 2014, 1077, 87.
- (9) Ha, T. *Methods* 2001, 25, 78.
- (10) Khan, Y. R.; Dykstra, T. E.; Scholes, G. D. *Chemical Physics Letters* 2008, 461, 305.

(11) Kobashi, H.; Morita, T.; Mataga, N. Chemical Physics Letters 1973, 20, 376.