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Light Harvesting Mechanism of Photosystem II in Photosynthesis:

An Inspiration to Photoinitiators¹

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Abstract: As one of the most important chemical reactions on the earth, the photosynthetic reaction has gained much attention. For example, foliage and algae possess superior abilities to harvest luminous energy from sunlight in photosynthetic reactions by capturing lights with the light-harvesting complex (LHC) and transferring the energy from LHC to the reaction center (RC) in Photosystem II (PSII), to realize the continuous and efficient transformation from luminous energy to chemistry energy. In this article, the progresses in the studies on the crystal structure of PSII, the energy and electron transfer mechanism, and artificial simulation on photo-induced electron transfer are reviewed. Additionally, the initiating mechanism of hydrogen-abstraction photoinitiators, and the inspiration of the principles and mechanisms of photo-induced electron transfer in macromolecular photoinitiators were also discussed. It is believed that properly choosing covalent chains of appropriate types and length as the bridge between electron donor and electron acceptor is crucial for improving the initiating efficiency of photoinitiators.

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1. INTRODUCTION

Photosynthesis has been attracting much attention for many years due to its superior ability of transforming luminous energy to the chemical energy of plants, algae and cyanobacteria, and many researches have been performed on the crystal structure of photosystem II, the mechanisms of energy and electron transfer, and relevant artificial simulation (Niels et al., 2000; Kamiya & Shen, 2003; Ferreira et al., 2004; Biesiadka et al., 2004; Nelson & Ben-shem, 2004; Standfuss et al., 2005). The major light-harvesting complex (LHCII) in Photosystem II (PSII) captures sunlight and transfer the energy to reaction centers (RC) for original charge separation, in which the luminous energy is transformed to electric energy. And then the electric energy is transformed to chemical energy by cells after a series of electric transfer processes. It is proved that the absorption, transfer and transformation of luminous energy in PSII are high efficient photo-physical or photo-chemical processes with the monochromatic incident photon-to-electron conversion efficiency (ICPE) up to 95% (Sundström & Van, 1999). These mainly profit from the efficient electron transfer of antenna system in PSII, which include LHC II and core antenna. From this, meaningful inspirations can be drawn onto the development of coatings.

As one of the polymers applied in waterborne UV-curable coatings, waterborne polyurethane acrylate (WPUA) has got developed rapidly owing to its environmental-friendliness, high curing rate and excellent flexibilities (Berg et al., 2008; BAI et al., 2007; Asif et al., 2005), and it has great potential in coatings, adhesives, electronic materials, textiles, leathers and printing inks (Kim et al., 2010). Therefore, WPUA is expected to replace solvent-based products and become the most favorable domestic and industrial coatings. However, the curing degree and performances of WPUA films largely depend on the initiating efficiency of photoinitiators, and when the films are thick or if pigments are added into WPUA, the casted films can not obtain sufficient crosslinking densities, impairing the adhesion force and mechanical properties of the products.

The high light-harvesting efficiency and ICPE of plants or algae give inspiration to the development of a novel kind of photoinitiator with improved initiating efficiency. For example, in the common hydrogen-abstraction photoinitiators, photosensitizers in photoinitiators get excited after absorbing the luminous energy, and then cause electron transfer between photosensitizers and co-initiators. This is similar to the photo-induced electron transfer process in photosynthesis. Therefore, it is quite worthy to investigate the ingenious light-harvesting mechanism and electron transfer mechanism in plants and then optimize the combining manner between the electron donor and the electron acceptor of hydrogen-abstraction photoinitiators. It is expected that the initiating efficiency of photoinitiators can be improved and the problem of deficient crosslinking densities of WPUA films can be solved.

2. ENERGY AND ELECTRON TRANSFER IN PSII

2.1 Crystal structure of PSII

The photosynthetic reaction happens under the coordinative functions of PSI and PSII. In this reaction, PSII is the start of the electron-transfer chains as well as the center of water splitting and oxygen emitting, and, therefore, PSII becomes the focus in the researches on photosynthesis. PSII is a complicated complex comprising outer light-harvesting complex (LHCII), core antenna complex (including CP43 and CP47), reactive center complex (RC) and Manganese cluster, and its components are so located and assigned as to ensure the quick and efficient energy and electron transfers.

The complicated configuration of PSII makes its crystal structure difficultly to be characterized, especially when the resolution is higher, and that makes it an internationally hot spot in relevant fields. In

these years, many researches have performed on the characterization and model building of crystal structures of LHC with a precision up to 3 Å in various living things, such as cyanobacterials, peas, spinaches and purple bacteriums, etc., and many studies on the artificial simulation of photosynthetic reactions and mechanisms of energy transfer have been rapidly carried out. In 2004, Liu et al (LIU et al., 2004) first reported the X-ray structure of spinach LHCII in icosahedral proteoliposome assembly at 2.72 Å resolution, and the chlorophyll (Chl) arrangement of trimeric LHCII is as shown in Fig. 1a. It was found that all 24 Chls from the stromal layer are organized into two irregular rings, and the average centre-to-centre distance between two neighboring Chls is about 11.26 Å, with the maximum 12.29 Å and minimum of 9.74 Å. As the energy transfer between two luminal clusters, which have longer distances, are much less efficient than those in a stromal layers, as presented in Fig. 1b, it was inferred that energy absorbed by the stromal Chls is quickly focused on Chla 612/Chla 611, and then transmitted to neighboring LHC or RC.

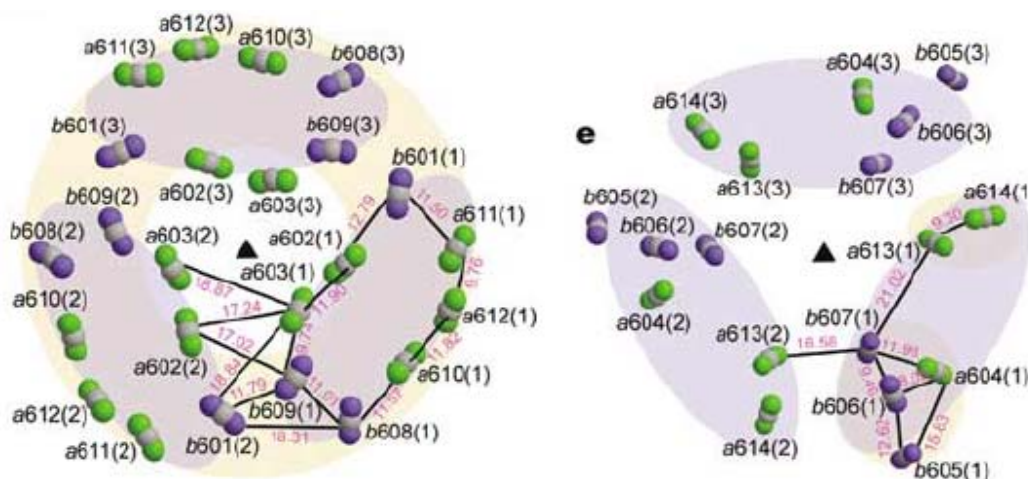


Fig.1: Chl arrangement of LHCII

Another researcher Loll et al (Loll et al., 2005) completed the crystal structure of PSII in *Thermosynechococcus vulcanus* in 3.0 Å, and Müh et al (Müh et al., 2008) reported the structures of antenna system and the small membrane-intrinsic subunits of cyanobacterial photosystem II at 3.0 Å resolution. These researches and progresses lay foundation for the further research on the energy and electron transfer mechanisms.

2.2 Energy transfer in PSII

In PSII, the antenna pigments and RC work together with the protein complex. The antenna subunits absorb the luminous energy and gets excited, and then transfers the energy to RC pigments for original photochemical reaction. It is considered that the energy transfer between the pigments can neither be attributed to molecule impact (because temperature cannot affect the original reactions), nor to the charge transfer between molecules. In fact it is because of the exciton transfer and resonance transfer.

Exciton is excited quanta which can transfer energy but not electron. When pigments are excited by luminous energy, the excitation is generated after electrons return to the former orbits, and then excites the neighboring pigment molecules, to complete a process of energy transfer. Resonance transfer utilizes electric vibrancy to transfer energy. When pigments are excited, the vibrancy of high energy electrons in them can cause the electric vibrancy of another neighboring molecule, through which energy gets transferred. In resonance transfer process, the energy donor and acceptor may either be the same molecules or different molecules.

The route of energy transfer is very complicated. It is generally believed that the core antenna complex CP43 and CP47 receive energy from outer LHCII system and assistant antennas, and then transfer the energy to RC complex to complete the energy transfer. However, the approach by which the antenna

pigments transfer the luminous energy to RC complex is still undetermined and disputed (Holzenburg et al., 1993; Beoekema et al., 1999; Boekema et al., 1999).

Barber et al (Nield & Barber, 2006) have utilized the published X-ray structures of a cyanobacterial PSII core, LHCII, PsbP and PsbQ proteins to construct a model of the plant LHCII-PSII supercomplex, as shown in Fig.2, and may spark the discussion on energy transfer approach. Fig.2a shows the LHCII-PSII supercomplex model with the cyanobacterial core and the spinach LHCII complex, and Fig.2b is of the Chls only. Ringed white is the closest Chl a pairing (LHCII-612 to CP43-11) with 17 Å that may facilitate energy transfer between LHCII and the PSII core.

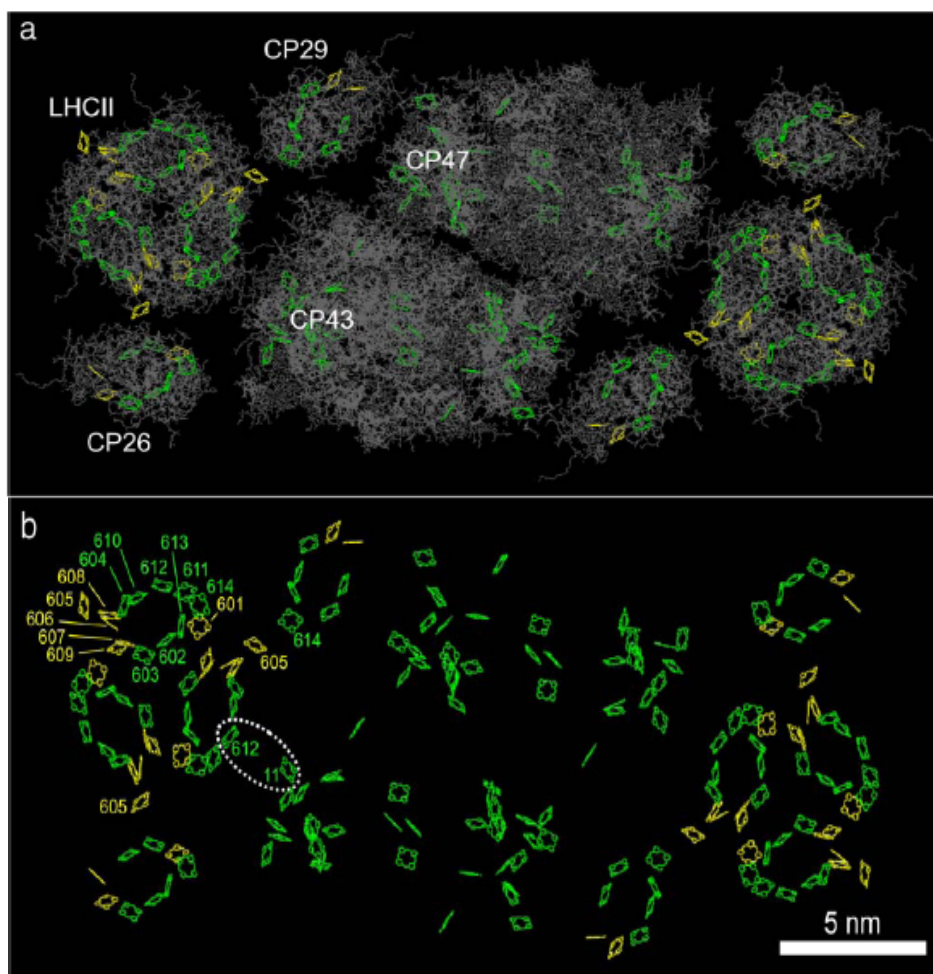
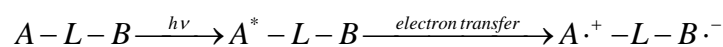


Fig. 2: The LHCII - PSII supercomplex mode

2.3 Electron transfer in PSII

When RC complex receives energy from antenna pigments in PSII, the original photochemical reaction happens and the electrons are transferred to other complexes. The electron transfer process can get explanation from Marcus Theory (Marcus, 1993). The supramolecular system participating in electron transfer can be expressed by A-L-B, where A and B are electron donor and electron acceptor respectively in electron transfer process and L is the “bridge” or coupling unit between A and B. This bridge can be covalent bonds or other forms, and the electron transfer process can be expressed as follows:



In original photochemical reactions, as the electron donor, the excited RC pigments transfer the electrons to electron acceptor to realize the charge separation and then leave behind "holes". After that, the RC pigments capture electrons from the secondary electron donor and return to the former state. Then the secondary electron donor also captures electrons from other electron donors until it captures electrons from the ultimate electron donor water. Similarly, the ultimate electron acceptor is NADP^+ , and the electron transfer carrier include PQ, Cyt b_6f complex, Fd and PC to realize the circulation of electrons in PSII.

3. INSPIRATION OF PHOTOSYNTHESIS

3.1 Macromolecular photoinitiator

The pigments-protein complexes in PSII, such as LHCII, RC, CP26 and CP 29, CP 43 and CP47, are assigned subtly, and the energy can be transferred through them for photochemical reactions because the distances between any two neighboring units are close enough (from 10 Å to 20 Å). However, in traditional hydrogen-abstraction photoinitiators, such as benzophenone/tertiary amine or thioxanthone/tertiary amine system, the photosensitizers and co-initiators are added into polymer and mixed physically without any coupling. As a result, the energy transfer efficiency of them will be restricted to a relative lower level because of the uniform distance between them and the low concentration. To solve this problem, designing a "bridge" between the photosensitizers and co-initiators like the photosynthesis pigments and confining them in small units like chloroplasts of plants can no doubt greatly improve the energy transfer efficiency and initiating efficiency of photoinitiators. In fact, there have been some researches on macromolecular photoinitiators coupling the photosensitive units and initiating units in a molecule (WEN et al., 2009; JIANG et al., 2004; Drozd et al., 1995; Ullrich et al., 2004), which increased the concentration of photoinitiator in certain area.

Yin et al (WANG et al., 2006; JIANG et al., 2005; JIANG et al., 2009; WANG et al., 2009; JIANG et al., 2005; WANG et al., 2007) developed a series of macromolecular photoinitiators by means of introducing the epoxy groups into thioxanthone, and coupling the tertiary amine with thioxanthone in a molecule through the reaction between epoxy and imine groups. Fig.3 shows the synthesis route of a novel macrophotoinitiator APTX taken by them. Compared with the photoinitiators without covalent coupling, APTX obtained higher initiating efficiency and had active effects on improving the unsaturation conversions of polymers.

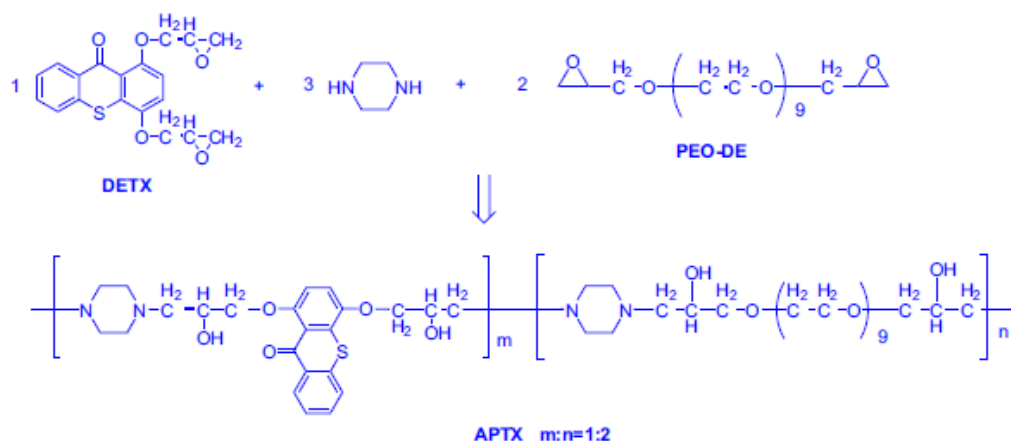


Fig. 3: The synthesis route of a novel macrophotoinitiator APTX

3.2 Bridge in electron transfer

The macromolecular photoinitiators have been developed fast recently and it has been proved that they can obtain higher initiating efficiency when photosensitive units and initiating units are coupled in a molecule

or a polymer chain than when in the physical mixture (Corrales et al., 2005). However, neither the length nor the type of the bridge between electron donor and electron acceptor considered as an important factor for improving the initiating efficiency. The bridge in macromolecular photoinitiators is usually controlled in a short distance though this will accelerate the anti process of electron transfer and shorten the charge separation life, resulting in a limitation on getting higher initiating efficiency.

It can be inferred from the antenna pigment structure and photochemical reactive process that the charge separation in plants is a long-range electron transfer process, and the bridge length is long enough to separate the charges. This is another important inspiration to the improvement of the initiating efficiency of photoinitiators. However, there have not been any reports on the bridge between photosensitive units and initiating units. To investigate the effect of bridge on electron transfer process, we can design a series of hydrogen-abstraction photoinitiators, such as thioxanthone/tertiary amine with different bridge lengths and types with thiosalicylic acid, phenols, diethylene triamine and isophorone diisocyanate, and the synthesis routes are as shown in Fig. 4. By using different raw materials or adjusting the chain length, we can synthesize molecules with different bridge types and lengths. In this photoinitiator, the thioxanthone groups can harvest luminous energy, performing the same function as that of the antenna pigments in LHC, and the energy can be transmitted to tertiary amine groups to activate photochemical reactions, like the RC in PSII. Besides, the WPUA can also transfer the energy and electron because of large amount of hydrogen bonds interactions among molecules, as the function of protein in PSII. To further optimize the initiating efficiency of photoinitiators, other factors, such as the molar ratio of thioxanthone/tertiary amine, the distribution of each constitute and the electric circular approach, should be investigated and optimized.

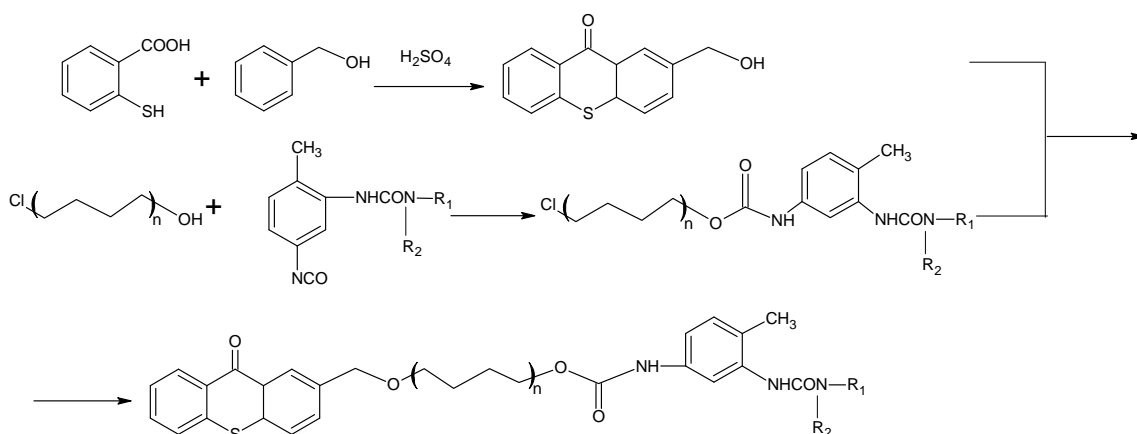


Fig. 4: Synthesis route of macromolecular photoinitiators with different bridge

4. CONCLUSIONS

Photosynthesis gives great inspirations to the improvement of the initiating efficiency of photoinitiators though further researches are still needed on light harvesting mechanism and the photochemical reactions between photosynthesis and photopolymerization reactions. The energy transfer and electron transfer mechanisms, together with the crystal structure of PSII, are introduced in this article, and the inspirations and design routes of novel macromolecular photoinitiators are discussed. It is proved by preparatory experiments that this idea is feasible and the new photoinitiator can initiate photopolymerization of WPUA efficiently. In addition, to investigate accurately the effect of bridge between photosensitive units and initiating units, a differential photo calorimeter (DPC) method should be utilized. It is expected that through further relevant research, the light harvesting ability and the initiating efficiency of photoinitiators can be greatly improved for practical applications.

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