Minireview

The history of photosynthetic thermoluminescence *

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Abstract

A fundamental discovery of photosynthetis research in the 1950s was the detection of thermally stimulated light emission from preilluminated photosynthetic material [Arnold W and Sherwood H (1957) Proc Natl Acad Sci USA 43: 105–114]. This phenomenon, called thermoluminescence (TL), is characteristic of a wide range of materials (minerals, semiconductors, inorganic and organic crystals, and complex biological systems), which share the ability of storing radiant energy in thermally stabilized trap states. The original discovery of TL in dried chloroplasts later proved to be a phenomenon common to all photosynthetic organisms: photosynthetic bacteria, cyanobacteria, algae and higher plants, which can be observed in isolated membrane particles, intact chloroplasts and unicellular organisms, and whole leaves. Following the initial observations considerable effort has been devoted to the identification and characterization of photosynthetic TL components. This work has firmly established the participation of various oxidation states of the water-oxidizing complex, the redox-active tyrosines, and the quinone electron acceptors of Photosystem II (PS II) in the generation of photosynthetic glow curves. Since TL characteristics are very sensitive to subtle changes in the redox properties of the involved electron transport components, the TL method has become a powerful tool in probing a wide range of PS II redox reactions and their modifications by environmental stress effects. Here, the main milestones of research in photosynthetic TL are covered until the present day.

Abbreviations: ADRY – agents *a*ccelerating the *d*eactivation *r*eactions of water-splitting enzyme *Y*; AG – afterglow; Chl – chlorophyll; DCMU – 3-(3,4-dichlorophenyl)-1,1-dimethylurea; DL and DLE – delayed light emission; PS I – Photosystem I; PS II – Photosystem II; TL – thermoluminescence; Tyr-D and Tyr-Z – redox active tyrosines of the PS II reaction center

Introduction

Thermoluminescence (TL) is a common and widespread phenomenon, which can be concisely described as emission of light at characteristic temperatures from samples that had been exposed to electromagnetic or particle radiation prior to their warming up in the dark (see Chen and Kirsh 1981). Besides, in several thousands of natural minerals, TL is observed in various artificially produced solid states, such as semiconductors, organic solids, metallo-organic compounds, and also in complex biological systems like the photosynthetic apparatus. A common feature of all TL phenomena is the storage of radiant energy in metastable trap states, which can be released via thermally stimulated radiative detrapping. The phenomenon of TL has been mentioned in alchemist texts as early as 1602 (see Arnold 1991), and its first scientific report was provided by Robert Boyle in an address to

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* Dedicated to William Archibald Arnold (December 1904– October 2001).

the Royal Society of London in 1663 describing it as 'glimmering light' which he observed from heating diamond in the dark (see Chen and Kirsh 1981). Scientific studies on the TL of minerals and other solid states started in the 1st quarter of the 20th century leading to the establishment of TL as an important method to study energy storage in thermally stabilized trap states.

Historically, photosynthetic TL research can be divided into three main periods: (i) Discovery of the phenomenon and primary characterization, which lasted from 1957 until end of the 1960s. (ii) Identification, characterization and assignment of the main TL bands to the redox components of the photosynthetic apparatus, from the beginning of 1970s until the end of the 1980s. (iii) Application of TL as a research tool to study photosynthetic electron transport under various physiological conditions. This period of research started roughly in the middle of 1980s and is currently still active until the recent days. Although the above periods are partly overlapping and represent only a rough division of research, they present a useful framework to provide an overview the main milestones of the process, which led to the establishment of TL as a versatile tool in photosynthesis research.

Discovery of the phenomenon and primary characterization

The initial boost leading to the discovery of TL in photosynthetic systems came through extrapolation of phenomenology from solid state research. Radiative detrapping occurs under isothermal conditions and the possibility to detect the emitted light, called delayed luminescence (DL; also called DLE, delayed light emission), depends on the detrapping rate at the particular temperature of observation. Thus, thermoluminescence is actually thermally stimulated delayed luminescence. The basic idea that part of the absorbed light energy is stored in the photosynthetic apparatus in long lived and remarkably stable trap states has been derived from the observation of delayed luminescence arising from chloroplasts by Bernard (Bernie) Strehler and William (Bill) Arnold (Strehler and Arnold 1951). 'So try to make glow curves from chloroplasts was obvious' as Arnold has recalled the first key moment in the history of photosynthetic TL (Arnold 1991). (See Figure 1 for a photograph of William Arnold.) The idea was not only obvious, but also successful and led to the discovery of TL from dried chloroplasts (Arnold

Figure 1. A photograph of William (Bill) Arnold, co-discoverer of thermoluminescence in plants (on the left) accompanied by C. Stacy French (middle) and Hans Gaffron (right). Photograph taken by Govindjee in Gattlinburg in 1972.

and Sherwood 1957), which was confirmed in the same year by Gordon Tollin and Melvin Calvin (Tollin and Calvin 1957). In the paper of Arnold and Sherwood, TL emission from leaf disks and the cells of the green alga *Chlorella* was also mentioned (Arnold and Sherwood 1957). However, due to technical difficulties arising from condensation on the optical components of water evaporated from the samples, TL curves from wet material were not presented. It was in 1966 when Arnold confirmed the presence of TL in intact cells of the *Chlorella* (Arnold 1966). These early results demonstrated that illuminated photosynthetic samples are able to store part of the light energy, which can be later re-emitted in a thermally activated manner. The experiments of Arnold, which were performed using various combinations of filters and photomultipliers with different spectral sensitivity, indicated that chlorophyll (Chl) is involved in the absorption and emission of light in the glow curves (Arnold and Sherwood 1957) providing strong support for the origin of TL from the light energy converting photosynthetic apparatus. For this and other discoveries, Govindjee et al. (1996) honored Arnold with a special issue of the *Photosynthesis Research*.

The initial hypothesis emerging from the discovery of TL and of DLE was that the photosynthetic apparatus behaves like semiconductors (Arnold and Sherwood 1957, 1959; Tollin and Calvin 1957). A simple generalized scheme of TL or DL emission based on the solid state model is shown in Figure 2. This model was later developed into an electron-hole picture of photosynthesis (Arnold 1965), in which a bound electron (to be used in the Calvin–Benson–
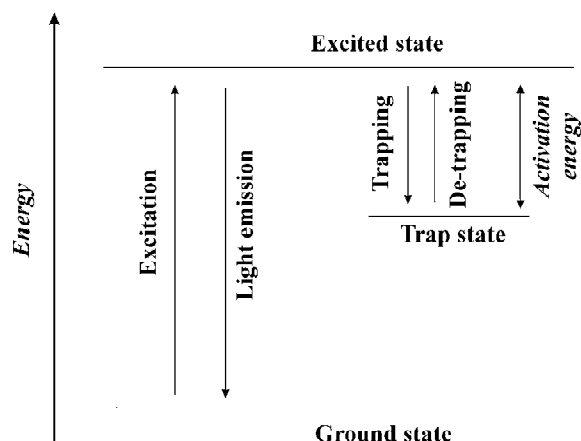
Figure 2. The generalized scheme of thermoluminescence (TL) and delayed light (DL) emission in solid states or other energy storage systems. After excitation by light or other radiation the system is converted from the ground state to the excited state. The excited state can decay back to the ground state via a radiative pathway producing prompt fluorescence, or can be stabilized in a metastable trap state. The trap is emptied via de-trapping, whose temperature dependent rate is determined by the activation energy. Radiative decay of the re-populated excited state leads to DL emission under isothermal conditions, and to TL emission under continuous heating of the sample, which thermally stimulates the de-trapping process.

Bassham cycle; see Bassham, this issue) and a free hole is formed in reaction center A (Photosystem (PS) I) as well as a bound hole (to be used in water oxidation) and a free electron is formed in reaction center B (PS II). According to the hypothesis of Arnold the recombination of the free hole (from PS I) and of the free electron (from PS II) would have been the mechanism for the production of delayed light and TL (Arnold 1966). The idea of free moving electrons and holes in a solid-state like photosynthetic apparatus was not supported by later experiments. Therefore, Arnold and Azzi (1968) postulated that both the positive and negative charge traps reside within the same photosynthetic unit, which is the water oxidizing System II (i.e., PS II). This proposal has been established as the basis for the interpretation of TL components related to photosynthetic activity. A scheme of the origin of photosynthetic TL arising from charge recombination in PS II is shown in Figure 3.

Identification, characterization and assignment of the main TL bands

Following the discovery of the phenomenon, development in instrumentation paved the way to the next important phase of photosynthetic TL research, which was devoted to the identification and basic characterization of the different TL bands. As a result of extensive studies a large amount of experimental data was accumulated on which the current understanding of photosynthetic TL was built up. These studies have been covered by detailed reviews (Inoue and Shibata 1982; Inoue 1983; Sane and Rutherford 1986; Horváth 1986; Demeter and Govindjee 1989; Vass and Inoue 1992; Inoue 1995; Vass and Govindjee 1996). Here, we will concentrate only on the main milestones.

Photosynthetic TL consists of several components

In the early TL experiments, Arnold's group observed that storage of the illuminated samples before the measurements decreases the TL intensity at the lower temperature part of the curve to a larger extent than at the higher temperature part. From this observation, they concluded that there are more than one energy storage states in the photosynthetic apparatus (Arnold and Sherwood 1957). This idea was later supported by glow curve measurements showing several peaks (Arnold and Sherwood 1959; Arnold 1966). Further studies have fully confirmed the existence of multiple energy storage states, and at least 10 different TL components have been identified from photosynthetic materials (see Table 1).

The temperature domain where photosynthetic TL can be observed is rather wide, starting from liquid He temperatures, through the -50 to $+50\,°C$ region where the most important photosynthetic TL components appear, up to $80–120\,°C$ where components from lipid peroxidation arise. During the years different nomenclatures were introduced for the identification of TL components. The nomenclature was more or less finalized by the mid 1970s in the form used until today, as summarized in Table 1. In order to make the list complete the table includes also the TL components, which were observed more recently.

TL components from photosynthetic material may be related or unrelated to photosynthetic activity

The work of Arnold and Azzi (1968), Andrej Rubin and Venediktov (1969), as well as Vladimir Shuvalov and Felix Litvin (1969) presented the first well-resolved TL curves from photosynthetic material. Rubin and Venediktov (1969) identified four peaks between -50 and $50\,°C$. (A photograph of Rubin appears in the paper by Belyaeva, this issue.) Arnold and Azzi (1968) and Shuvalov and Litvin (1969) induced the TL curves by illumination at liquid nitrogen
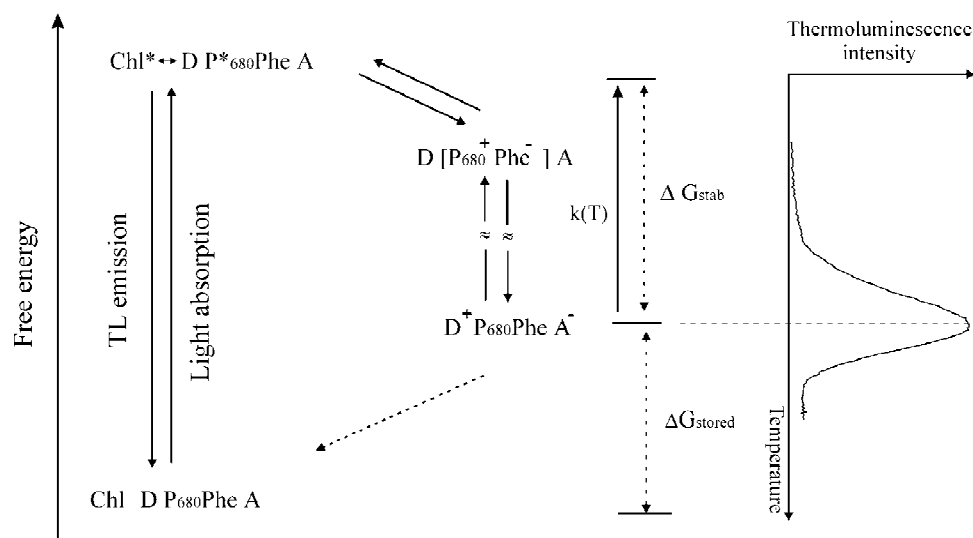
Chl* ↔ D P*$_{680}$Phe A

Thermoluminescence
intensity

D [P$_{680}^+$ Phe$^-$] A

ΔG_{stab}

k(T)

D$^+$P$_{680}$Phe A$^-$

ΔG_{stored}

Chl D P$_{680}$Phe A

Free energy

TL emission

Light absorption

Temperature

Figure 3. The scheme of thermoluminescence (TL) emission arising from Photosystem II (PS II) via charge recombination. After light absorption by chlorophylls the primary photoreaction produces charge separation between P680 and pheophytin (Pheo). The separated charges are stabilized on secondary donors (D), such as the charge storage states of the water-oxidizing complex or the redox active tyrosines, and acceptors (A), such as the first, Q_A, and second, Q_B, quinone electron acceptors. The charge separation process is reversible, which leads to a temperature dependent reexcitation of P680 and antenna chlorophylls, whose light emitting de-excitation leads to TL emission. The charge separated state is stabilized by the free energy loss, ΔG_{stab}, which approximately equals the free energy of activiation ($\Delta G^{\#}$) required for radiative recombination of the particular charge pair. The free energy stored by the separated charge pair, ΔG_{stored}, is given by the difference of the photon energy and ΔG_{stab}. The dashed arrow indicates non-radiative charge recombination pathway(s). The peak position and the shape of the TL band is determined by $\Delta G^{\#}$, i.e., higher peak position corresponds to higher $\Delta G^{\#}$ (ΔG_{stab}).

Table 1. The peak temperature and origin of photosynthetic TL bands

TL component	Peak temperature (°C)	Origin/charge pair
Low temperature bands[1]	−250, −220, −200	Energy storage in aggregated Chls[1]
Z-band[2]	∼ −160	Chl$^+$(?) Chl$^-$ (?)[3]
Zv-band[4]	Variable (−80 to −30)	P$_{680}^+$(Chl$^+$?) Q_A^{-}[5]
A-band[6]	∼−15	Tyr-Z$^{\cdot}$$Q_A^{-}$[7]
A$_T$-band[8]	∼−15	His$^+$ Q_A^{-}[9]
Q-band[10]	∼+5	$S_2Q_A^{-}$[11]
B$_1$-band[12]	∼+30 to +40	$S_2Q_B^{-}$[13]
B$_2$-band[12]	∼+30	$S_3Q_B^{-}$[13]
C-band[6]	∼ +50	Tyr-D$^{\cdot}$$Q_A^{-}$[15]
AG-band[16]	∼+40−50	$S_{2(3)}Q_BX^{-}$[16]
High temperature bands[17]	∼+50 to +70	Oxidative chemiluminescence[18]
High temperature bands[19]	∼+130 to 140	Lipid peroxidation[19]

The references given as superscripts in the first column refer to the observation of the components, whereas the references indicated as superscripts in the third column refer to the interpretation of their origin. [1](Noguchi et al. 1992), [2](Arnold and Azzi 1968; Shuvalov and Litvin 1969), [3](Sonoike et al. 1991), [4](Ichikawa et al. 1975; Desai et al. 1977), [5](Vass et al. 1989; Chapman et al. 1991), [6](Rubin and Venediktov 1969; Desai et al. 1975; Inoue 1981), [7](Demeter et al. 1985a), [8](Inoue et al. 1977; Rózsa and Demeter 1982), [9](Ono and Inoue 1991; Kramer et al. 1994), [10](Rubin and Venediktov 1969; Lurie and Bertsch 1974a), [11](Rutherford et al. 1982). If DCMU is added after the excitation the $S_3Q_A^{-}$ recombination also results in the Q band (Demeter et al. 1982)), [12](Arnold and Azzi 1968; Rubin and Venediktov 1969; Lurie and Bertsch 1974a; Inoue 1981), [13](Rutherford et al. 1982; Inoue 1983; Demeter and Vass 1984), [14](Rubin and Venediktov 1969; Desai et al. 1975), [15](Demeter et al. 1993; Johnson et al. 1994), [16](Miranda and Ducruet 1995) The electron source (X$^-$) for this band is related to reversed electron flow around PS II, [17](Sane et al. 1977; Rózsa et al. 1989; Hideg and Vass 1992), [18](Vass et al. 1989; Hideg and Vass 1993), [19](Ducruet and Vavilin 1999).

temperature and identified a band at around $-160\,^{\circ}\mathrm{C}$, called the Z band, besides the peaks appearing at higher temperatures. They have shown that the Z band can be observed not only in photosynthetically active preparations, but also in extracted pigment solutions, indicating that storage of absorbed light energy in pigment assemblies without charge transfer events is the main mechanism behind these components. Shuvalov and Litvin (1969) have also observed TL bands in the temperature range of -15 to $+40\,^{\circ}\mathrm{C}$, which could be associated with the functioning of PS II. Subsequent work by Ichikawa et al. (1975) confirmed that in leaves and isolated chloroplasts most of the TL bands disappear after inactivation of oxygen evolving activity; however, a band at around $50\,^{\circ}\mathrm{C}$ could be observed in inactive material as well.

TL components from Photosystem II

Ichikawa et al. (1975) demonstrated that the Z_V, Q, B_1 and B_2 TL bands, which appear between -80 and $40\,^{\circ}\mathrm{C}$, are dependent on photosynthetic activity since they are not observed in boiled or etiolated leaves. Although the work of Arnold and Azzi (1968) postulated that radiative charge recombination may take place in PS II, but not in PS I, one of the basic questions in relation to the origin of TL was: which of the two photosystems is responsible for the bands related to photosynthetic activity. The experiments obtained with inhibitors of electron transport (Rubin and Venediktov 1969; Desai et al. 1975), mutants (Arnold and Azzi 1968) and various subchloroplast particles (Lurie and Bertsch 1974a; Sane et al. 1977) showed that the Q, B_1 and B_2 bands arise from PS II. These findings were later fully confirmed by detailed studies including high resolution measurements of spectral distribution of the emitted light (Sonoike et al. 1991).

Having established that PS II is the main, if not the only source of TL, which is related to photosynthetic electron transport the next problem to solve was the identification of positive and negative charge storage sates, which participate in the thermally stimulated charge recombination process. The identification of the reservoir of positive charges was initiated by the observations of the group of Kazuo Shibata and Yorinao Inoue showing that the major TL bands were missing in dark-grown gymnosperm leaves, or angiosperm leaves greened under widely spaced intermittent illumination (Ichikawa et al. 1975; Inoue et al. 1976), as well as in algae cells grown in Mn-deficient medium (Inoue 1976). (See Figure 4 for photographs

of Kazuo Shibata and Yorinao Inoue.) When the latent water-oxidizing complex in the above systems was photoactivated by continuous light or closely-spaced flashes, the Q, B_1 and B_2 bands were induced, which indicated that the oxidation states of the water-oxidizing complex are involved in the generation of TL (Ichikawa et al. 1975; Inoue 1976; Inoue et al. 1976). This idea was confirmed by observing a period-four oscillation in the intensity of the B band when it was excited by single turnover flashes (Inoue and Shibata 1977b), which could be simulated by assuming that charge recombination involved the S_2 and S_3 oxidation states of the water-oxidizing complex (Rutherford et al. 1982, 1984; Inoue 1983; Demeter and Vass 1984). (For historical accounts of period 4 oscillations in Chl fluorescence, see Delosme and Joliot 2002; and in oxygen evolution, see P. Joliot, this issue.)

The first hint for the identity of the negative charge reservoir came from the observations of Rubin and Venediktov (1969), who found the interconversion of two TL components corresponding to the B1 and Q bands, by DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea), a chemical that inhibits electron transport at the acceptor side of PS II. Although the mechanism of DCMU action, i.e., that it blocks the electron transport between the Q_A and Q_B quinone electron acceptors, was not known at that time the DCMU effect was used to support the involvement of a negatively charged acceptor component of PS II in TL emission. This observation was extended by a number of studies on the effect of various electron transport inhibitors acting at the acceptor side of PS II (Lurie and Bertsch 1974a; Ichikawa et al. 1975). Demeter et al. (1979) were the first to relate the DCMU induced induction of the Q band and the concomitant suppression of the B(B1) band to the participation of the semireduced first quinone electron acceptor Q_A, which was called at that time Q, in the generation of the Q band. (See Figure 4 for a photograph of Sándor Demeter.) The participation of the semireduced secondary quinone electron acceptor, $Q_B{}^-$, in the generation of the B band was clarified by the elegant work of Bill Rutherford and his co-workers (1982) in which single turnover flashes were used to excite TL. (See Figure 5 for a photograph of Bill Rutherford.) These experiments confirmed also that $Q_A{}^-$ is the source of electrons for the charge recombination reaction resulting in the Q band. Thus, the work of Rutherford et al. (1982) made clear that the Q band originates from the $S_2 Q_A{}^-$ recombination, and iden-

Figure 4. Photographs of Kazuo Shibata (upper left), Yorinao Inoue (upper right, 2000), Sándor Demeter (middle left), Gábor Horváth (middle right), Don DeVault (lower left, 1989) and Prafullachandra Vishnu (Raj) Sane (lower right). Shibata's photograph was provided by Andrew Benson.

Figure 5. William (Bill) Rutherford (left) during a discussion with Johannes Messinger (middle) and Julian Eaton-Rye (right). A 1999 photograph taken by Govindjee, at a Gordon Conference.

tified the B band as originating from the $S_2Q_B^-$ and $S_3Q_B^-$ recombinations. Typical TL curves showing these bands are depicted in Figure 6. The role of Q_B^- in the B band was further supported by the experiments of Demeter et al. (1982), in which the ratio of the oxidized and semireduced Q_B populations was modified in the samples. At neutral pHs the $S_2Q_B^-$ and $S_3Q_B^-$ recombinations give rise to identical bands in terms of peak temperature and shape; however, at lower pHs (4.5-6.0) TL from the two recombinations is split into the $B_1(S_2Q_B^-)$ and B_2 $(S_3Q_B^-)$ bands, which are separated by about 10–15 °C temperature difference (Inoue 1981).

The involvement of the positively charged oxidation states of the water-oxidizing complex as well as of semireduced Q_A and Q_B in the Q and B bands has been firmly established by early 1980s. [Figure 7 shows part of the group in the RIKEN (Rikagaku Kenkyushu) institute in Japan, which was actively participating in this field of TL research.] Clarification of the origin of the Z_V, A and C bands, which are also related to photosynthetic electron transport took a longer time although the involvement of Q_A^- as the negatively charged recombination partner in all of these components had been proposed after their discovery. The identification of the positive charge reservoirs was more controversial and eventually Chl^+ (or P_{680}^+) (Vass et al. 1985, 1989), Tyr-Z· (Demeter et al. 1985a) or another organic radical like His^+ (Ono and Inoue
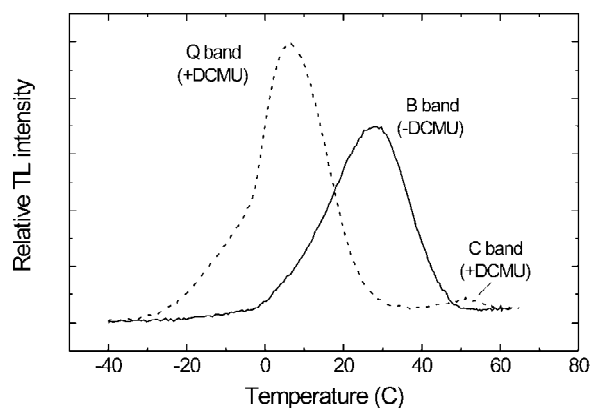

Figure 6. Typical TL curves measured in the absence and presence of DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea) in *Synechocystis* 6803 cells. Single flash illumination of untreated cells results in the B band of TL, whereas in the presence of DCMU the Q, as well as the C band is observed.

1991; Kramer et al. 1994) and Tyr-D· (Demeter et al. 1993b; Johnson et al. 1994b) have been shown or proposed to participate in the Z_V, A and C bands, respectively.

TL components from Photosystem I

Besides the unambiguous establishment of PS II as the main source of photosynthetic TL it was also proposed that a component at around 50 °C arises from PS I since it could be induced by 740 nm light (Desai et al.

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Figure 7. Some members of the Solar Energy Group in the RIKEN Institute, Wako-Shi, Saitama, Japan, that was one of the leading centers of photosynthetic TL research. The picture was taken in 1986, and shows from left to right: Taka-Aki Ono, Hiroyuki Koike, Yorinao Inoue, Mamiko Kimimura (secretary), Tatsuo Omata and Imre Vass.

1975). Although this hypothesis was not confirmed, recently a TL component, called the AG (afterglow) band, has been identified, which originates from PS II, but modulated by cyclic electron transport around PS I in leaves illuminated by far-red light (Miranda and Ducruet 1995). It is also of note that TL components, which are unrelated to photosynthetic electron transport are emitted from PS I, which seem to originate from energy storage in the antenna pigment system (Sonoike et al. 1991; Noguchi et al. 1992) or light emission by oxidative chemiluminescence (Hideg and Vass 1993).

TL components unrelated to photosynthetic activity

In addition to the TL components which arise from charge recombination in PS II, further bands were observed at low temperatures, at $-160\,^{\circ}$C (Arnold and Azzi 1968; Shuvalov and Litvin 1969) or between -250 and $-160\,^{\circ}$C (Noguchi et al. 1992), which are related to energy storage in the pigment assemblies of PS II and PS I. Although energy dissipation mechanisms were studied by utilizing low temperature TL measurements (Hagen et al. 1995), the mechanisms underlying this type of TL emission have not yet been clarified. TL components can be observed also in the non-physiological high temperature range of 70 to 120–130 $^{\circ}$C. These include a band at around 70 $^{\circ}$C,

which is suggested to originate from oxidative chemiluminescence of protein bound pigments (Hideg and Vass 1993), and a band above 100 $^{\circ}$C, which is related to lipid peroxidation processes (Vavilin et al. 1991; Ducruet and Vavilin 1999).

TL from photosynthetic bacteria

TL emission can also be observed from photosynthetic bacteria. Darell Fleishman (1971) found two TL peaks under aerobic conditions, and one peak at around 20 $^{\circ}$C under anaerobic conditions in the purple bacterium *Rhodopseudomonas viridis*. The 20 $^{\circ}$C band was suggested to arise from the recombination of $P_{960}{}^{+}$, the oxidized primary donor, with a reduced secondary acceptor, probably $Q_B{}^{-}$ (see Sane and Rutherford 1986). (Photographs of Prafullachandra Vishnu Sane and Bill Rutherford are shown in Figures 4 and 5, respectively.) Govindjee et al. (1977) reported TL from *Rhodopseudomonas sphaeroides*, which was proposed to arise from magnesium protoporphyrin IX, a precursor of bacteriochlorophyll. In contrast to the popularity of TL in probing PS II electron transport, it has not yet developed into a frequently applied method in photosynthetic bacteria. This is mainly due to the very low yield of TL emission and the lack of stabilized charge pairs, which could recombine via the radiative pathway.

Mathematical description of photosynthetic TL

The characteristic temperatures where the peak of TL emission is observed are determined by the energetic depth of the trap states. As a rule of thumb, the higher the peak temperature of a TL band the deeper the energetic stability of the related trap (provided that the experimental conditions, especially the heating rate, are the same).

Despite the non-complete correspondence of the photosynthetic apparatus to solid states in terms of the electronic band structure of semiconductors, the basic features of photosynthetic TL can be described in the framework of the simple model that has been developed by Randall and Wilkins (1945) to explain TL from solid states. The Randall Wilkins model was used to calculate activation energies without modification (Arnold and Sherwood 1959; Arnold and Azzi 1968; Lurie and Bertsch 1974b; Tatake et al. 1981) and was later generalized for biological systems (Vass et al. 1981; deVault et al. 1983). It is important to note that the shape and peak temperature of a TL band is not determined by the activation energy (more precisely activation enthalpy) alone. Full description of the energetics of charge recombination and the related TL component requires the free energy of activation (ΔG^*), which reflects the redox potential difference of the stabilized charge pair. The work of Don deVault and Govindjee (see DeVault et al. 1983, and deVault and Govindjee 1990) provided a theoretical background for the approximation of the multi-step recombination with a hypothetical single step. (Photographs of Don deVault and Govindjee are shown in Figures 4 and 8, respectively.) They have shown that the free energy of activation, that can be calculated from a TL band assuming a single step recombination, approximately equals the sum of the free energies of the involved equilibrium reactions plus the free energy of activation for the final $P_{680}^+Ph^-$ recombination. However, the correct calculation of the entropy contribution is hampered not only by the multi-step recombination process, but also by the extent of adiabacity of the final recombination step. In case of a non-adiabatic electron transfer the calculated entropy may be underestimated. Despite its simplicity and limitations, this approach resulted in good predictions for the stabilization free energies and room temperature halftimes of different charge pairs of PS II (see Vass et al. 1981; Vass and Inoue 1992).

The Randall–Wilkins type treatment of TL results in so-called first order kinetic bands, which show an asymmetric band shape, with the high temperature part of the curve being steeper than the low temperature part. This feature has been observed in several isolated systems, like spinach thylakoids, but in intact systems such as whole cyanobacterial cells, the TL bands are more symmetric, which indicates a deviation from the first order kinetics. This question has been addressed by Pandit Vidyasagar and his co-workers, who used general order kinetic curves (Vidyasagar et al. 1993; Thomas et al. 1996), which, however, do not have a clear physical/physiological meaning in regard to photosynthetic electron transport. More recently Esa Tyystjärvi and Imre Vass (2004) have proposed that the alteration from first order kinetics can be explained by assuming that the trap states are represented by distribution of energy levels instead of a well defined single activation energy.

A further refinement in the description of photosynthetic TL may be needed due to the existence of non-radiative processes, which empty the trap states in competition with the radiative, TL producing recombination. The original hypothesis of such a pathway (Vass and Demeter 1983) has recently gained experimental support showing that direct charge recombination in the PS II complex, which is expected to proceed via electron tuneling between Q_A^- and P_{680}^+ (Rappaport et al. 2002), can affect the shape, peak position and intensity of the Q band (Vavilin and Vermaas 2000).

TL as a research tool in photosynthesis

The main redox components that participate in TL emission are the reduced forms of the Q_A and Q_B quinone electron acceptors, the S_2 and S_3 redox states of the water-oxidizing complex, Tyr-D· and Tyr-Z· (Table 1). Consequently, TL provides a powerful tool to monitor the function and activity of the above redox components in various plant material ranging from isolated PS II reaction center complexes through PS II enriched membranes and thylakoids to intact leaves and whole cells of cyanobacteria or algae.

The functioning of Photosystem II redox components

The participation of the S_2 and S_3 states of the water-oxidizing complex in the B band has been very useful to study S-state turnovers. A particular advantage was the ability to monitor individual S-state transitions, as well as changes in the energetic stability. This

Figure 8. A photograph showing László Kálmán, Govindjee, Robert Bittle, Jim Allen and Imre Vass. A 1999 photograph taken at a Gordon Conference.

approach has been applied to study the temperature dependence of the particular S-state transitions (Inoue and Shibata 1977; Koike and Inoue 1987); the effect of the so-called ADRY agents (Agents *A*ccelerating the *D*eactivation *R*eactions of water-splitting enzyme *Y*) in destabilizing the higher S states (Renger and Inoue 1983); the effects of water analogs on the S-state turnovers (Ono and Inoue 1988; Vass et al. 1990); the role of the inorganic cofactors in the S-state cycling, for Mn^{2+} (Inoue et al. 1977; Ono and Inoue 1985; Hegde and Padhye 1990), Ca^{2+} (Ono and Inoue 1989; Krieger et al. 1998; Ono 2000), and Cl^- (Homann et al. 1986; Homann 1993; Krieger et al. 1998); the function of the extrinsic polypeptides associated with the water-oxidizing complex (Ono and Inoue 1985; Vass et al. 1987; Homann and Madabusi 1993); and the participation of histidine residues in water oxidation (Banerjee and Vidyasagar 1990; Ono and Inoue 1991; Hegde et al. 1993; Kramer et al. 1994).

Another field of successful applications covered the function of the Q_A-Q_B two-electron gate. Various electron transport inhibitors, including agriculturally important herbicides, like atrazine and diuron, block the Q_A^- to Q_B electron transfer step, which results in the conversion of the so-called B band into the Q band. Based on this phenomenon the TL method was utilized in clarifying the mode of action of different inhibitors (Demeter et al. 1982; Vass and Demeter 1982), testing and identifying new chemicals and potential herbicides (Asami et al. 1988; Koike et al. 1989; Kovács et al. 1996; Horváth et al. 1996; Govindjee et al. 1997; Bock et al. 2001). Recently the modification of the

Q_B binding site by phosphatidyl glycerol was also supported by TL data (Gombos et al. 2002). This field of TL research was reviewed by Gábor Horváth (Horváth 1986), whose photograph is shown in Figure 4.

A related area of research was the mechanism of herbicide resistance. A number of naturally selected or genetically created mutants are known, which exhibit increased resistance against various herbicides acting at the Q_B site. These mutants have one or more amino acid changes in the Q_B binding region, which decreases not only herbicide binding but in many cases also the binding affinity of Q_B and the energetic stability of Q_B^-. This latter effect results in the shift of the B band to lower temperatures that can be conveniently studied by TL and can be used to identify and characterize herbicide resistant biotypes (Demeter et al. 1985b; Etienne et al. 1990; Gleiter et al. 1990, 1992). The sensitivity of the TL method is well demonstrated by the fact that a 50–70 mV redox potential difference between the Q_B/Q_B^- and Q_A/Q_A^- couples results in about 25–30 °C difference in the peak temperature of the corresponding B and Q bands (Demeter et al. 1985b). A further application of TL concerning acceptor side characteristics was the study of protonation events at or around the Q_B site. The upshift of the B_1 band, arising from the $S_2Q_B^-$ recombination, at low pH is assigned to protonation induced stabilization of Q_B^-, providing an approach to study protonation effects (Rutherford et al. 1985; Vass and Inoue 1986). This topic is also related to the effect of bicarbonate in modifying electron transport between Q_A and Q_B as well as the protonation of Q_B^- (Govindjee et al.

Figure 9. A group photo of the joint US–Hungarian workshop, which was held in Szeged, Hungary in 1983. Numbering of the rows is from bottom to top, and the names in the rows are listed from left to right (not mentioned): 1st row: G. Dastageer, Gyözö Garab, Abdul Rashid, József Géza Kiss, Géza Meszéna; 2nd row: Tatjana Szitó, James Barber, Lawrence Bogorad, Ágnes Faludi-Dániel, Alexander A. Krasnovsky, Mrs. Gibbs, Martin Gibbs, Elisabeth Gantt, Mrs. San Pietro; 3rd row: Éva Sárvári, Béla Böddi, László Mustárdy, Clanton Black, Ervin Latzko, Samuel Beale, Károly Csatorday, Áron Keresztes, Anthony San Pietro, Charlie Arntzen; 4th row: György Paless, Gábor Erdös, Zoltán Szigeti, Tóth Gábor, János Hevesi, Péter Maróti, Achim Trebst, Sándor Demeter, László Szalay, Szeréna Maróti, Imre Maróti, Geoffrey Hind, Govindjee, P. Vaishnav, Györgyi Muschinek, Klára Barabás.

1984; Sane et al. 1984; Garab et al. 1988; Demeter et al. 1995). Applications of TL in studying photosynthetic electron transport was included in discussions during a joint US-Hungarian workshop in 1983, whose participants are shown in Figure 9.

Due to its applicability in intact systems, TL has proven a useful method of probing PS II activity in intact leaves (Rutherford et al. 1984; Krieger et al. 1993; Johnson and Krieger 1994; Miranda and Ducruet 1995), or in lichen thalli (Sass et al. 1996). With the development of genetic engineering techniques in studying structure-function relationships of PS II electron transport, various algal and cyanobacterial mutants have been constructed. TL was especially suitable to characterize the function of PS II in such mutants since it could be applied in intact cells without the need of time consuming and costly isolation procedures (see, e.g., Vass et al. 1992; Burnap et al. 1992; Mayes et al. 1993; Gleiter et al. 1994; Nixon et al. 1995; Mäenpää et al. 1995; Vavilin and Vermaas 2000; and Hatano-Iwasaki et al. 2001).

Damage of the photosynthetic apparatus by environmental stress factors

Since PS II is a sensitive site of the photosynthetic apparatus, which is affected by various environmental factors, TL has become a powerful tool in studying the damaging mechanisms of a number of environmental effects. These include the mechanism of photoinhibition by visible light (Vass et al. 1988; Ohad et al. 1988, 1990; Keren et al. 1995; Briantis et al. 1996; Misra et al. 1997) and ultraviolet radiation (Desai 1990; Hideg et al. 1993; Turcsányi and Vass 2000). The mode and site of action of heavy metals, like Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} (Mohanty et al. 1989a, b; Horvath et al. 1998) and acclimation to elevated (Govindjee et al. 1985) and low temperatures (Janda et al. 2000), as well as to desiccation (Sass et al. 1996; Takács et al. 1999; Skotnica et al. 2000) were also studied. More recently TL measurements gained important applications in characterization of the consequences of oxidative stress (Hideg and Vass 1993; Stallaert et al. 1995; Marder

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et al. 1998; Ducruet and Vavilin 1999; Havaux and Niyogi 1999).

Concluding remarks

Studies on the phenomenon of photosynthetic TL during more than 45 years since its discovery have clarified the origin of many TL components, and proved the usefulness of the TL method in the studies of many of the redox reactions in PS II. This method has the advantage of a relatively simple instrumentation and easy applicability to study almost all redox components of PS II in intact and isolated systems. It is expected that the useful and informative TL method will keep helping us in exploring a number of current and future problems of photosynthesis research in the years to come.

Acknowledgments

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