

Evolution of the Z-scheme of photosynthesis: a perspective

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Abstract The concept of the Z-scheme of oxygenic photosynthesis is in all the textbooks. However, its evolution is not. We focus here mainly on some of the history of its biophysical aspects. We have arbitrarily divided here the 1941–2016 period into three sub-periods: (a) Origin of the concept of two light reactions: first hinted at, in 1941, by James Franck and Karl Herzfeld; described and explained, in 1945, by Eugene Rabinowitch; and a clear hypothesis, given in 1956 by Rabinowitch, of the then available cytochrome experiments: one light oxidizing it and another

reducing it; (b) Experimental discovery of the two light reactions and two pigment systems and the Z-scheme of photosynthesis: Robert Emerson's discovery, in 1957, of enhancement in photosynthesis when two light beams (one in the far-red region, and the other of shorter wavelengths) are given together than when given separately; and the 1960 scheme of Robin Hill & Fay Bendall; and (c) Evolution of the many versions of the Z-Scheme: Louis Duysens and Jan Amesz's 1961 experiments on oxidation and reduction of cytochrome *f* by two different wavelengths of light, followed by the work of many others for more than 50 years.

Submitted for publication in honor of Nathan Nelson, a world leader in the field of photosynthesis, and of T. Nejat Veziroglou, a world leader in the field of hydrogen evolution (see Tsygankov et al. 2016; also see pdfs at <http://www.life.illinois.edu/govindjee/honorsfrom.html>).

John Raven sent the following comment on this paper: “The history of the concept of the ‘Z scheme’ analysed in this manuscript by Govindjee and colleagues is timely and accurate. The sequence of publications cited, and the discussion of these publications, show how theoretical and experimental work led to our present concept of linear electron transport in oxygenic photosynthesis”.

Electronic supplementary material The online version of this article (doi:10.1007/s11120-016-0333-z) contains supplementary material, which is available to authorized users.

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The main purpose of this educational paper is to provide an overview of the origin of the concept of the two light reactions and two photosystems that has evolved during the last 75 years. Obviously, the evolution of this concept into the modern Z-scheme (as we know it today) did not take

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forms of Chl *a* through absorption spectroscopy (also see Krasnovsky 1992). In view of the fact that Emerson's experiments were made with manometry that cannot distinguish between light-induced changes in oxygen evolution (photosynthesis) and oxygen uptake (respiration), it was important to prove that the effect was not in respiration. This was achieved by inhibiting respiration by parabenzoquinone, which then also acted as electron acceptor instead of CO₂; using this method, R. Govindjee et al. (1960) showed that the two-light effect was not in respiration, but in the Hill reaction (the light reaction phase of photosynthesis). This laid to rest the idea by Lawrence Rogers Blinks (1957, 1959) (b.1900–d.1989; see Abbott and Smith 2010) that the two-light effect may have been in respiration. In addition to the two light effect in photosynthesis, an “antiparallel” two light effect was discovered in Chl *a* fluorescence, as expected (Govindjee et al. 1960), studied soon thereafter, by e.g., Duysens and Sweers (1963). For further discussion on what information Chl *a* fluorescence has provided to the two light reaction two pigment system concept, see chapters in: Papa-georgiou and Govindjee (2004) and in Demmig-Adams et al. (2014). Further, the Emerson enhancement effect was confirmed, by mass spectrometry, to be in photosynthesis (Govindjee et al. 1963), as well as by the existence of Emerson enhancement effect in NADP reduction in chloroplasts (Govindjee et al. 1964). *The scene was set soon thereafter* (see Nickelsen 2015).

A major event at that time was the publication of the famous highly cited and recognized paper by Hill and Bendall (1960) [see Bendall (1994) for an article on Robert (Robin) Hill (1899–1991)]. Based on thermodynamic arguments, a theoretical Z-scheme was published, where, one light reaction (now I) oxidized a Cyt *f* and another light reaction (now II) reduced Cyt *b*₆, and ATP was produced due to energy available from the downhill electron transfer from reduced Cyt *b*₆ to Cyt *f* (see Fig. 2). Although Hill and Bendall (1960) did not relate this scheme to Emerson's discovery and to the concepts of Eugene Rabinowitch, and although the Cyt *b*₆ in this scheme is not the one involved as suggested, this scheme was powerful in its impact; it tied all things together. We note that Robin Hill was indeed a major discoverer; see two excellent articles on him as well as on the Z-Scheme by Walker (2002a, b). We, however, recognize that the idea of two light reaction and two pigment system was “in the air” so to say, and discussed in several publications (see above), and in Kok (1959); and in papers presented, during March 28–31, 1960, by Rabinowitch and Govindjee (pp. 378–586); B. Kok and G. Hoch (pp. 397–416); R. Hill and W.D. Bonner (424–435); C.S. French (pp. 447–471); and D.I. Arnon (pp. 489–565)] at a symposium on “Light and Life” held at the Johns Hopkins

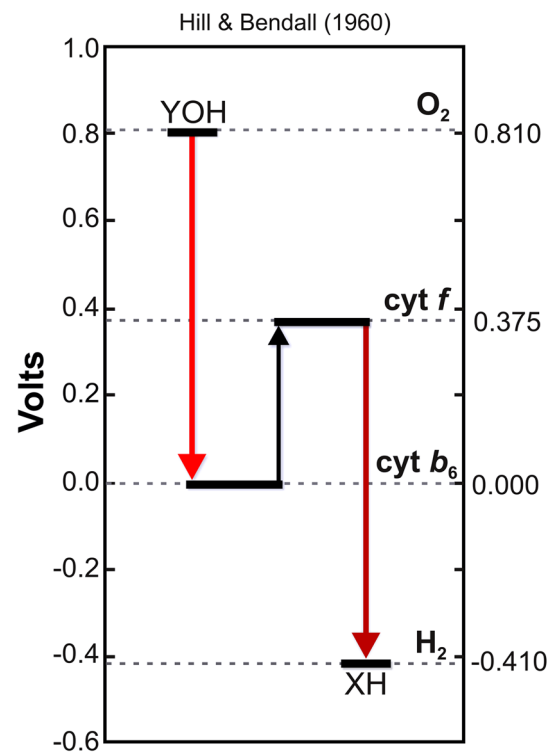


Fig. 2 The two light reaction scheme of Hill and Bendall (1960). The figure was drawn with the water/oxygen system at the top, rather than the other way around, as is done currently to show that the light reaction is an uphill process. In the light reaction related to current photosystem II, a reductant “Y” reduces oxidized Cytochrome (Cyt) *b*₆ becoming YOH, and reducing Cyt *b*₆ (we now know that Cyt *b*₆ does not play this role). In the other light reaction, Cyt *f* reduces an intermediate “X” to “XH”. What was really new in this scheme was that electron flow from reduced Cyt *b*₆ to oxidized Cyt *f* would be a thermo-chemically downhill process, and, thus, having the potential of making ATP just as happens in mitochondria. The diagram shown here was redrawn from the original Fig. 4 of Hill and Bendall (1960)

University; see McElroy and Glass (1961). Hill (1965) presented a detailed and thorough review on the electron transport chain, especially on the Z-scheme of photosynthesis, but, unfortunately, he missed citing Emerson's and Rabinowitch's key papers, on the concept of two light reactions and two pigment systems, cited here.

Evolution of the many versions of the Z-scheme: 1961—the present

The most crucial experiment that clinched the series scheme of photosynthesis was that of Louis N. M. Duysens et al. (1961) who showed an antagonistic effect of light I and II on the redox state of Cyt *f*; Duysens and coworkers first added “red light” to a suspension of red alga *Porphyridium*, and thus, it was *light 1*: it oxidized Cyt *f*; however, when they added the second beam of light, *light 2*, oxidized

Cyt *f* was reduced! Thus, the names *Light I*, *Light II*, *Pigment System I*, *Pigment System II*, *Light Reaction I*, *Light Reaction II*, *Photosystem I (PSI)* and *Photosystem II (PSII)* came into being (also see Duysens and Ames 1962; Duysens 1989; Govindjee and Pulles 2016)! A lesser-known, but an important, experiment that had preceded this experiment was that of Bessel Kok (1918–1979; see Kok 1959; Myers 1987), where he observed that in a cyanobacterium far-red light oxidized the reaction center P700 that he had discovered earlier (Kok 1956, 1957), and a shorter wave light reduced this oxidized P700. Both the photosystems (I and II) as well as both the reaction centers (P700 in PSI; and P680 in PSII) contain Chl *a*, but these different Chl *a*'s have different properties and functions since they are bound differently to different proteins (see Björn et al. 2009 for a perspective).

In this historical minireview, we are not going to discuss the details of the Z-scheme except that we mention the discovery of the reaction center of PSII, P680, by the research group of Horst T. Witt (1922–2007; see Döring et al. 1968; Govindjee et al. 1970; also see; Witt 2004); for early speculations, see Krey and Govindjee (1964) and Rabinowitch and Govindjee (1965), and the discovery of pheophytin function as one of the “primary” electron acceptors of PSII (Klimov et al. 1977, and reviews by; Klimov 2003; and, Mamedov et al. 2015). Today, there are many versions of the Z-scheme, but we show here just a few: a 1965 scheme by Rabinowitch and Govindjee (Fig. 3); another (Fig. 4) by Blankenship and Prince (1985), where they had, in our opinion, correctly included P680, P680*, P700 and P700* as participants in the scheme, and had discussed why excited singlet state potentials of the chlorophylls should be included. We note that even at that time some textbooks (see e.g. Parson 1983) and research papers (Prince et al. 1976; Parson and Monger 1976) had this information in schemes on “anoxygenic photosynthesis”, but more relevant to this paper, on oxygenic photosynthesis were the schemes of Witt (1971), and that of Govindjee and van Rensen (1978). Figure 5 is a simplified scheme of Govindjee and van Rensen (1978) and Fig. 6 is a detailed scheme in the form of “Z-” (modified from Demeter and Govindjee 1989, which was based partly on Fig. 11 in Govindjee and Govindjee 1975). See Supplementary Material for additional figures.

We refer the readers to Mohapatra and Singh (2015) and Jaiswal et al. (2016) to see how the Z-scheme can be taught to students, through drama, outdoors, and indoors, respectively. In addition, for school children, a simple and fun video (DVD), with rap music is available (see: <http://www.biologymusicvideos.com/biol-o-gee-rap-photosynthesis.html>).

Further, we mention four things of special interest to all of us: (1) In addition to linear electron flow from water to

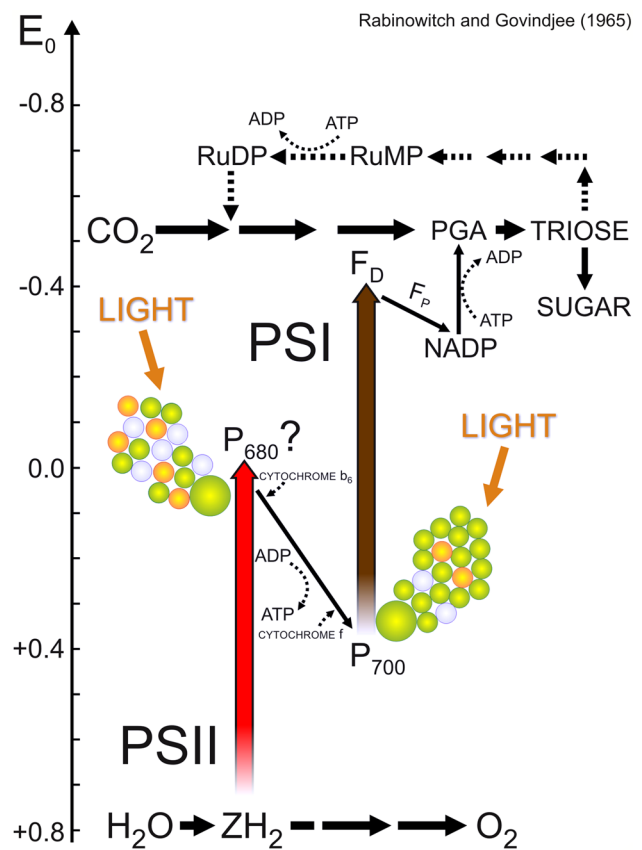
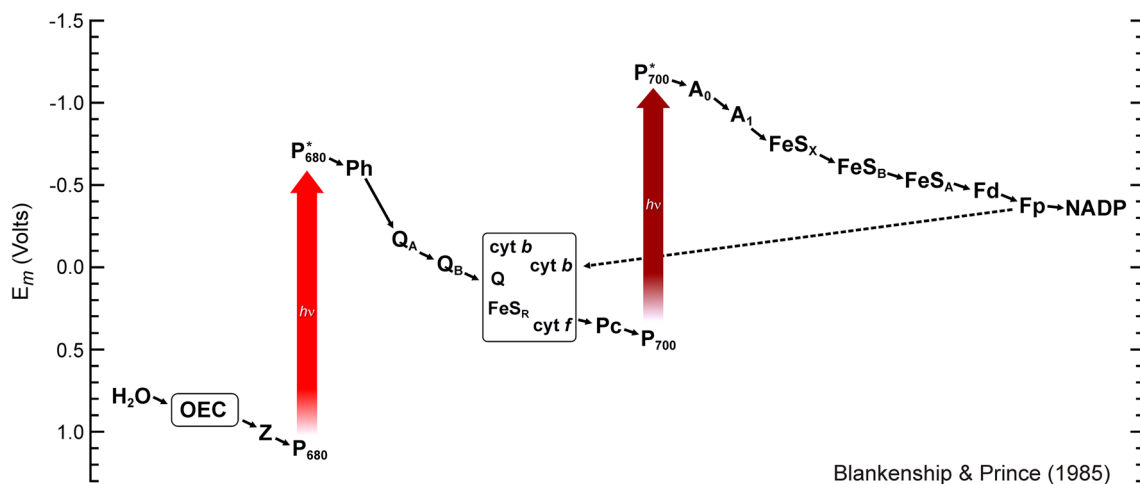


Fig. 3 A 1964–1965 scheme of two light reactions (I and II) and two photosystems (PSI and PSII), which included basic reactions of Calvin-Benson cycle, and of the possible existence of “Trap II”, listed as “P680?” before its discovery by Döring et al. (1968) in Horst Witt’s lab in Berlin (also see Govindjee et al. 1970). ZH_2 is the electron donor to the reaction center (or “Trap II”), whereas P700 is “Trap I”, discovered by Kok (1956, 1957). In retrospect, P680, and the PSII antenna should have been placed close to water. F_D stands for ferredoxin, F_P for a flavoprotein, NADP for nicotinamide dinucleotide phosphate, PGA for phosphoglyceric acid, RuMP and RuDP (now RuBP) for ribulose mono and di (or bi) phosphate. This diagram was made by Govindjee (1964, unpublished; see Krey and Govindjee 1964), and drawn by Natalie H. Davis, an artist in the then Department of Botany, University of Illinois at Urbana-Champaign (UIUC). It was first published by Rabinowitch and Govindjee (1965). [A photograph of Wolfgang Junge with the original 1964–1965 diagram pointing to P680 is in the Supplementary Material (also see a pdf on Junge at <http://www.life.illinois.edu/govindjee/honorsfrom.html>)]

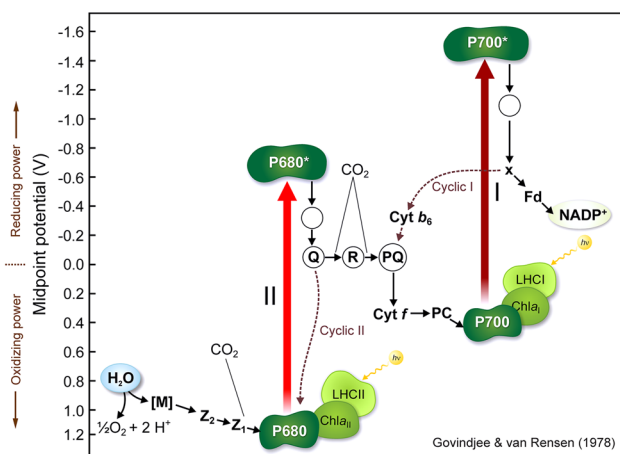
$NADP^+$, there exists a “Q” cycle involving Cyt *b₆f* complex, which brings extra protons to the thylakoid lumen, providing greater amount of proton motive force (pmf) to make more ATP molecules per electron transferred (see e.g., Crofts 2004; Dumas et al. 2016, and chapters in; Cramer and Kallas 2016). (2) In almost all plants, there also exists a cyclic electron flow around PSI leading to ATP formation (see e.g., Finazzi and Johnson 2016; Shikanai 2016). (3) Oxygenic photosynthesis uniquely requires bicarbonate ions (hydrogen carbonate) bound on non-heme



Blankenship & Prince (1985)

Fig. 4 A colored (redrawn) version of the Z-scheme from Blankenship and Prince (1985). The redox carriers were placed according to the accepted midpoint redox potentials (pH 7). *OEC*: oxygen evolving complex, *Z*: electron donor to photosystem II (PSII), *P₆₈₀*: reaction center chlorophyll (*Chl a*) of PSII, *Ph*: pheophytin, *Q*: quinone, *Cyt*: cytochrome, *FeS_R*: Reiske iron-sulfur protein, *Pc*: plastocyanin, *P₇₀₀*: reaction center *Chl a* of photosystem I (PSI), *A₀* and *A₁*: primary elec-

tron acceptors of PSI, *FeS_x*, *FeS_B*, and *FeS_A*: bound iron-sulfur protein acceptors of PSI, *Fd*: soluble ferredoxin, *Fp*: flavoprotein (ferredoxin-NADP reductase). In this diagram, electron transfer through the redox components of plastoquinone pool and *Cyt b₆f* complex is not shown. The dashed line indicates cyclic electron transfer around PSI. [Note that in the current literature some of the redox components of the Z-scheme use different abbreviations.]



Govindjee & van Rensen (1978)

Fig. 5 A simplified (redrawn) and colored version of the Z-scheme from Govindjee and van Rensen (1978). Following Witt (1971), this was the first detailed “visualization” of the excited singlet states of reaction center chlorophylls of photosystem II (PSII) and photosystem I (PSI) (P680 and P700) on top of excitation arrows (light red for PSII and dark red for PSI). Note that the knowledge about photosynthesis at that time was not complete for locating all (presently known) redox cofactors of electron transfer chain into this scheme. For original abbreviations of all shown components, see the detailed legend to Fig. 1 in Govindjee and van Rensen (1978); also see the legend of Fig. 6

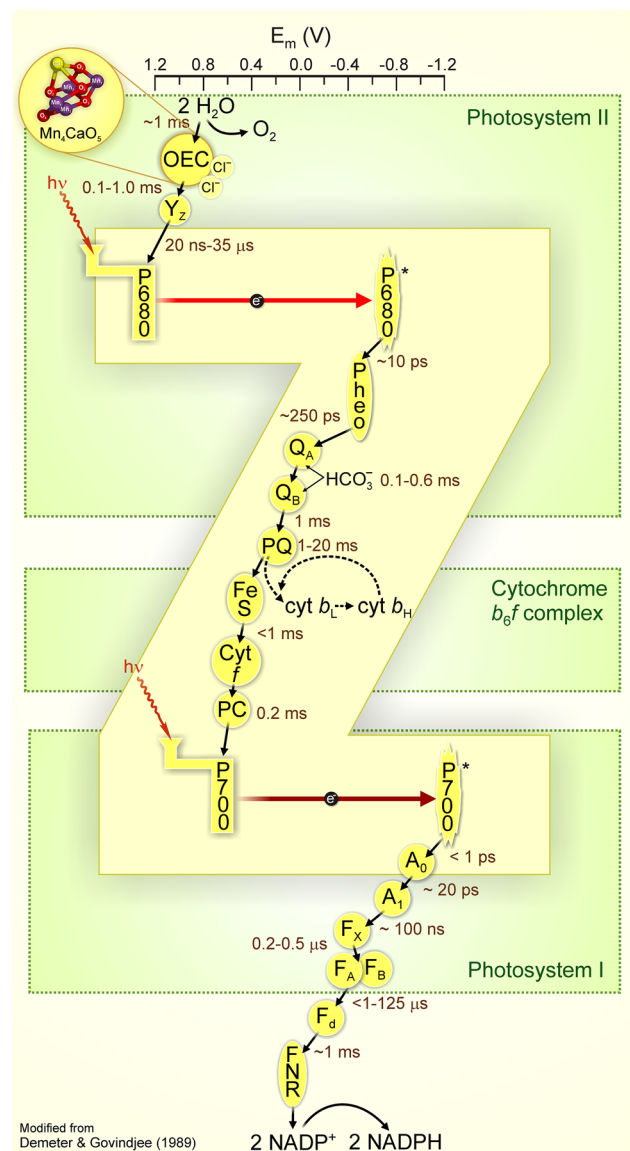
iron between the first and the second plastoquinone electron acceptors *Q_A* and *Q_B*, and this bicarbonate is essential for electron and proton transfer at the *Q_B* site (Wydrzynski and Govindjee 1975; Eaton-Rye and Govindjee 1988; Brinkert et al. 2016; and a review by; Shevela et al. 2012).

Moreover, bicarbonate is also known to have effects on the water-splitting side of PSII (Stemler et al. 1974); unbound bicarbonate ions, on this side, may act as proton acceptors (see e.g., Ananyev et al. 2005; Shutova et al. 2008; Shevela et al. 2013; Koroidov et al. 2014), or participate in photoassembly (Allakhverdiev et al. 1997; Baranov et al. 2004; Dasgupta et al. 2008), or stabilize the water-oxidizing complex (Klimov et al. 1997, 2003), but not to act as a substrate for oxygen evolution (see e.g., Clausen et al. 2005; Hillier et al. 2006). (4) It is of paramount importance to realize that the very first steps that start the photochemistry in oxygenic photosynthesis is the primary charge separation at the reaction center I (P700) and the reaction center II (P680), and that these charge separation events occur within picosecond (10^{-12} s) time scale (see e.g., early papers by Wasielewski et al. 1987, 1989; and reviews by; Mamedov et al. 2015; Milanovsky et al. 2014; Nadochenko et al. 2014).

Shevela and Govindjee (2016) have produced a detailed poster of oxygenic photosynthesis; it is available free: at http://www.life.illinois.edu/govindjee/Electronic%20Publications/2016_Poster-Shevela_Govindjee.pdf. It includes the oxygen-evolving manganese clock (see e.g., Joliot and Kok 1975); the ATP synthesis clock (see e.g., Mitchell 1961; Abrahams et al. 1994; Boyer 1997; Jagendorf 2002; Junge 2004); the two-electron gate for plastoquinone reduction (see e.g., chapters in Wydrzynski and Satoh 2005); and the carbon reduction cycle, the Calvin-Benson cycle (see e.g., Benson 2002; Bassham 2003).

We end this perspective with the news that tremendous progress has now been made in understanding both the

Fig. 6 The Z scheme of electron transport in photosynthesis. The electron carriers are placed horizontally according to their midpoint redox potentials at pH 7.0 (E_m 7). A slightly modified version of the original 1989 figure legend follows. Electron flow is initiated when a photon or exciton reaches the reaction center Chl *a* P680 (in PS II) and P700 (in PS I) (see $h\nu$ going into the two funnels). P680* and P700* (see distorted ovals) indicate the first singlet excited states of P680 and P700. The *first* reaction of P680* is the conversion of excitonic energy into chemical energy: charge separation, i.e., the formation of the cation P680⁺ and the anion (Pheo⁻) within ~10 ps (a chlorophyll before pheophytin has been left out). [For information on pheophytin, see Allakhverdiev et al. 2010.] The first reaction of P700*, the charge separation into P700⁺A₀⁻, may need <1 ps. Here, A₀ is a special Chl *a* molecule. The P680* recovers its lost electron from Y_Z, tyrosine-161 of the D1 polypeptide of PSII. The positive charge on Y_Z is then transferred to the charge accumulator Mn₄CaO₅ cluster, or the oxygen-evolving complex (OEC). Four positive charges must accumulate before an O₂ molecule is evolved. The Pheo⁻ delivers the “extra” electron to a primary (plastoquinone) electron acceptor, Q_A located on the D2 polypeptide of PSII; Q_A⁻ delivers its electron to a secondary (plastoquinone) electron acceptor O_B⁻ located on the D1 polypeptide of PSII. After reduction to plastoquinol, i.e. after two turnover of the P680, Q_B(H₂) exchanges with a mobile plastoquinone (PQ) molecule. Bicarbonate ions (HCO₃⁻) are now known to be involved in the Q_A-Fe-Q_B region, where Fe is a non-heme iron atom between the two plastoquinones. Plastoquinol (PQH₂) delivers one electron to the Rieske iron-sulfur protein (FeS), and the other to a Cyt_b_L. The electron on reduced FeS reduces Cyt *f*, and the one on Cyt *b*_L is transferred to Cyt *b*_H, returning back in a cyclic process (called the Q-cycle). Reduced Cyt *f* delivers its extra electron to a copper protein, plastocyanin (PC), which delivers the electron to P700⁺ (produced in the primary PSI reaction). On the other hand, A₀ passes its electron to A₁ (a phylloquinone molecule). The rest of the electron carriers are: F_X, F_A, and F_B (iron sulfur clusters), Fd (ferredoxin) and FNR (ferredoxin-NADP⁺ reductase). The diagram shows either measured or estimated times of the various reactions in the Z-scheme, except for the production of P680* and P700* that occur in femtosecond time scale. The bottleneck reaction is of the order of 5 ms and it involves the total time involved in the exchange of Q_B(H₂) with PQ; and the diffusion of PQH₂ to the Cyt *b*₆*f* complex, and the reoxidation time of PQH₂ (modified from Fig. 2 in Demeter and Govindjee 1989)



photosystems at atomic level resolution, and it is obvious to us that we are now very close to understanding both the physics and chemistry of excitation energy transfer as well as photochemical reactions in both photosystems since atomic level crystal structures of both PSI and PSII are now available. Even before this, Crofts et al. (1987) and Xiong et al. (1996), among others, had obtained atomic level PSII structure, based on homology modeling with the bacterial reaction centers [see Xiong et al. (1998) for a detailed review]. Now, high resolution (1.9–3.5 Å) structures of PSII are available, not only for thermophilic cyanobacteria (Umena et al. 2011; Shen 2015; Suga et al. 2015; Young et al. 2016), but also for red algae at 2.76 Å resolution (Ago et al. 2016), and for higher plants at 3.2 Å resolution (Wei et al. 2016) (Fig. 7). As a starting point, readers are referred to the following publications, particularly on PSII: Amunts et al. (2007); Barber (2016); Cox et al. (2014); Mukherjee et al. (2012), Najafpour

et al. (2012, 2013); Nelson and Junge (2015); Qin et al. (2015); Vinyard et al. (2013); and Zhang et al. (2015). *The future of our knowledge about photosynthesis looks very bright.* This paper is a good example of how fast our knowledge can evolve just within several decades. For information on just a few selected leaders in the field, see presentations at: <http://www.life.illinois.edu/govindjee/honorsfrom.html>.

Readers are encouraged to consult Walker (1992a, b); and books by Rabinowitch and Govindjee (1969), Ke (2001), Blankenship (2014), and in the near future a book by Björn et al. (forthcoming). For further discussion on different aspects of photosynthesis, see various volumes in *Advances in Photosynthesis and Respiration* (<http://www.springer.com/series/5599>), including those edited by Ort and Yocum (1996; on Oxygenic Photosynthesis),

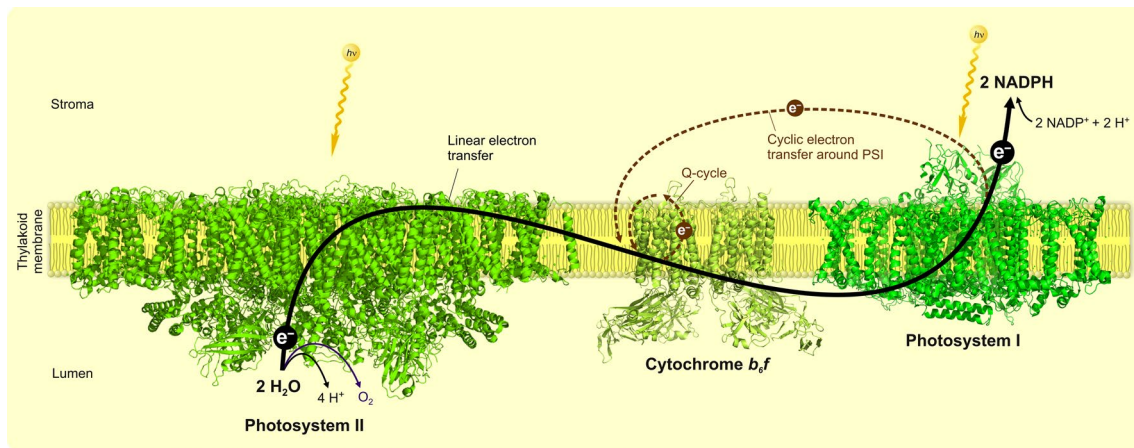


Fig. 7 Overall side-on view of the three major multiprotein photosynthetic complexes (PSII, Cyt b_6f , and PSI), located in the thylakoid membrane; they contain (or bind) the redox components (not shown) required for linear electron flow from H_2O to NADP^+ (**bold black arrow**). The higher plant (spinach) dimeric PSII-LHCII supercomplex was generated using coordinates of cryo-EM structure at 3.2 Å depos-

ited at Protein Data Bank (PDB) as ID 3JCU (Wei et al. 2016). The dimeric Cyt b_6f complex of the thermophilic cyanobacterium *Mastigocladus laminosus* was generated from a 3.0 Å crystal structure deposited at PDB as ID 1VF5 (Kurisu et al. 2003). The higher plant (spinach) PSI-LHCI supercomplex at 2.8 Å resolution was produced employing coordinates from PDB, using ID 4Y28 (Mazor et al. 2015)

Wydrzynski and Satoh (2005; on Photosystem II), Govindjee et al. (2005; on Discoveries in Photosynthesis), Golbeck (2006; on Photosystem I), Eaton-Rye et al. (2012; on Overviews on Photosynthesis) and Cramer and Kallas (2016; on Cytochromes).

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Appendix

The following example shows that science is a self-correcting enterprise, no matter who the authors are, and that even the top scientists make mistakes. James Franck, together with Gustav Ludwig Hertz, received the 1925 Nobel Prize in Physics in 1926 for “for their discovery of the laws governing the impact of an electron upon an atom”. Later, he became known for the “Franck–Condon Principle”, which states that upon light absorption, a molecule goes into an excited state, but in a higher vibrational

state. (See Rice and Jortner (2010) for all the major contributions, and life, of Franck.) Franck contributed extensively to photosynthesis (see Rosenberg 2004; also see Franck and Rosenberg 1964). Unfortunately, some of his thoughts, which may have been physically sound, turned out to be incorrect. Examples are: instead of using realistic 3-dimensional structure of the “antenna”, Franck and Teller (1938) calculated excitation energy transfer as if the pigments were located in one dimension; with these results, they challenged the concept of “photosynthetic unit”, but when two-dimensional and multidimensional approaches were used, their conclusions could not be accepted (see e.g., Bay and Pearlstein 1963; Robinson 1967). In the same manner, explanation by Franck (1958) of the “red drop” (Emerson and Lewis 1943) and the Emerson Enhancement Effect (Emerson et al. 1957), by double excitation (“up-conversion”) of the same chlorophyll *a* molecules was also incorrect.

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