8. Zusammenfassung

Phytochrome sind Photorezeptoren, die seit langem aus Pflanzen bekannt sind und die in den letzten Jahren auch in Cyanobakterien, nicht photosynthetischen Bakterien, Pilzen und Algen gefunden wurden.

Die photochromen Eigenschaften der Phytochrome sind durch die reversible Konvertierung zwischen dem Rotlicht-absorbierenden P_r-Zustand und dem Dunkelrotlicht-absorbierenden P_{fr}-Zustand charakterisiert. Die Photokonversion wird durch den lichtabhängigen Schritt, die Z/E-Isomerisierung der 15,16-Doppelbindung des Bilinchromophors, eingeleitet.

Die Stereochemie der C/D-Methinbrücke des Biliverdin Chromophors in Agp1 aus *Agrobacterium tumefaciens* konnte durch Verwendung von arretierten Bilinanaloga bestimmt werden. So besitzt der Chromophor in der P_r-Form die Stereochemie 15Za und in der P_{fr}-Form die Stereochemie 15Ea. Damit konnten weitere Änderungen der Stereochemie der C/D-Methinbrücke während der Photokonversion ausgeschlossen werden. Die fehlenden Absorptionsänderungen bei Blitzlichtmessungen und die starke Fluoreszenz des 15Za-Adduktes von Agp1 demonstrierten, dass die Z/E Isomerisierung durch die Arretierung verhindert wird.

Dichtefunktionalrechnungen haben vorhergesagt, dass es während der P_r/P_{fr}-Photokonver-sion zur Änderung der Stereochemie der A/B-Methinbrücke kommt. Die in dieser Arbeit durchgeführten Untersuchungen mit dem 5Zs-Addukt von Agp1, bei dem die A/B-Methin-brücke des Chromophors in der 5Zs Geometrie arretiert war, bestätigen diese Vorhersage nicht nur, sondern es konnte bestimmt werden, dass diese Änderungen während der Meta-R_C-Bildung stattfinden müssen. Auf diese Weise konnte ein weiterer Schlüsselschritt der P_r/P_{fr}-Photokonversion identifiziert werden.

Die CD-Spektroskopie im sichtbaren Bereich liefert wichtige Informationen über die Chiralität des Chromophors. Der Vergleich von CD-Spektren verschiedener Phytochrome und verschiedener Bilin-Addukte von Agp1 zeigte, dass der Chromophor im P_r Zustand immer dieselbe Chiralität besitzt. Die Chiralität wird dabei durch das konjugierte π-System des Chromophors und der Ausdehnung über den Chromophor bestimmt. Bei pflanzlichen Phytochromen und bei Cph1, die Phytochromobilin (PΦB) bzw. Phycocyanobilin (PCB) als natürlichen Chromophor besitzen, kommt es während der P_r/P_{fr}-Photokonversion zu einem Vorzeichenwechsel der Q-Bande im CD-Spektrum. Dieser Vorzeichenwechsel kommt nach der in dieser Arbeit aufgestellten Arbeitshypothese durch die Z/E-Isomerisierung der 15,16-Doppelbindung des Chromophors zustande die zur Umkehrung der Chiralität führt. Bei den nicht kovalenten PCB- und PΦB-Addukten und dem kovalenten BV-Addukt von Agp1wurde in der Q-Bande kein Vorzeichenwechsel beobachtet, sondern die Rotationsstärke in der P_{fr}-Form ist annähernd null. Dies wird mit einer Änderung der Stereochemie der A/B-Methinbrücke erklärt die zur Entgegengesetzten Chiralität der C/D-Methinbrücke führt, was letztendlich zur Kompensation beider Signale führt. Bei kovalent gebundenem PCB und PΦB kommt es nicht zur Kompensation, da in diesem Fall der Ring A des Chromophor nicht mehr am π-System partizipiert. Diese Modellvorstellungen sollen durch weitere Untersuchungen bestätigt und erweitert werden.

Auf den lichtabhängigen Schritt der P_r/P_{fr}-Photokonversion folgen eine Reihe thermischer Relaxationen bei denen einige spektral unterscheidbare Intermediate durchlaufen werden und die von strukturellen Änderungen des Chromophors und des Proteins begleitet werden.

Die Kinetik der P_r/P_{fr}-Photokonversion des BV-Adduktes von Agp1 wurde mit Blitzlichtspektroskopie untersucht. Im Wesentlichen ist die Kinetik denen der pflanzlichen Phytochrome sehr ähnlich und es wurden drei Intermediate identifiziert, die aufgrund der analogen spektralen Eigenschaften, wie die der pflanzlichen Phytochrome mit Lumi-R, Meta-R_A und Meta-R_C bezeichnet wurden.

Die kinetischen Untersuchungen mit dem Agp1 Addukt des 18EtBV Chromophors zeigten, dass die Kinetik durch die Vinylgruppe an Position 18 von BV verlangsamt wird. Die beschleunigte Kinetik des 18EtBV Adduktes ist wohl auf die höhere Flexibilität der Ethylgruppe gegenüber der Vinylgruppe zurückzuführen. Die Identifizierung von Aminosäuren der Bindungstasche die zu Verlangsamung führen ist Thema weiterer Studien. Ein Kandidat ist die konservierte Aminosäure Y166 deren Substitution durch Alanin nicht nur zu einer Verlangsamung führte sondern bei der auch die Meta-R_C-Bildung über zwei spektrale Übergänge verläuft.

Die Kinetik der P_r/P_{fr}-Photokonversion von Agp1 schließt mehrere ratenbegrenzende Protonentransferschritte ein, wie die gefundene pH-Abhängigkeit der Meta-R_C und P_{fr} Bildung und der große Deuteriumisotopeneffekt der Meta-R_A und Meta-R_C Bildung zeigen. Resonanz Raman Messungen zeigten, dass der Chromophor in Meta-R_C im Gegensatz zu P_r und P_{fr} deprotoniert vorliegt. Dies stimmt hervorragend mit der Abgabe eines Protons bei der Meta-R_C-Bildung und der anschließenden Protonenaufnahme bei der P_{fr}-Bildung überein. Da auch bei Cph1 ein ähnliches Muster der Protonierungsänderung beobachtet wurde, kann davon ausgegangen werden, dass die transiente Deprotonierung des Chromophors und die Protonenabgabe ein Schlüsselschritt der strukturellen Änderungen und der finalen P_{fr}-Bildung ist.

Die Kristallstrukturen der P_r-Form der CBD von DrBphP aus Deinococcus radiodurans und RpBphP3 aus Rhodopseudomonas palustris zeigten, dass der protonierte Chromophor durch mehrere Wasserstoffbrücken mit Aminosäuren der Bindungstasche stabilisiert wird. Die Substitution zweier dieser Aminosäuren D197 und H250 von Agp1, die streng konserviert sind, durch Alanin führte zu einer Verminderung des pK-Wertes des protonierten Chromophors im Vergleich zum WT. Weiterhin führte die Beleuchtung mit rotem Licht weder bei D197A noch bei H250A zur Bildung von P_{fr}. Das gebildete Photoprodukt von H250A zeigte mehrere Übereinstimmungen mit dem Intermediat Meta-R_C des WT auf. Bei D197A ist zurzeit noch nicht klar was für ein Photoprodukt nach Beleuchtung mit rotem Licht gebildet wird. Auf jeden Fall zeigen die Daten, dass beide Aminosäuren, wie aufgrund ihres Konservierungsgrades zu erwarten war eine entscheidenden Rolle bei der P_{fr}-Bildung spielen. Im Falle von D197 könnte diese aus der Kopplung des protonierten Chromophors mit der PHY-Domäne bestehen.

Wie die Untersuchungen mit dem M20 Fragment zeigen, bei dem die PHY-Domäne fehlt, ist die PHY-Domäne an der Ausbildung des P_{fr}-Zustandes entscheidend beteiligt. Dies ist überraschend, da die PHY-Domäne selbst nicht an der Chromophorbindungstasche beteiligt ist. Die Kinetik von M20 nach Anregung des Dunkelzustandes, der der P_r-Form stark ähnelt, zeigt große Abweichungen zu der des WT. Das gebildete Photoprodukt wiederum zeigte spektral viele Gemeinsamkeiten mit dem Meta-R_C Intermediat, weshalb davon ausgegangen wird, dass es Meta-R_C ähnlich ist. Die genaue Rolle der PHY-Domäne ist Thema weiterer Untersuchungen.

Agp1 bildet auch mit nicht kovalent gebundenem BV ein photochromes Addukt aus, wie die Untersuchungen mit der Punktmutante C20A zeigten. Dabei kommt es zu charakteristischen spektralen Unterschieden im Vergleich zum kovalent gebundenen BV-Addukt. Auf diese Weise wurde festgestellt, dass der Chromophor im M15Δ18N Konstrukt, bei dem die Aminosäuren 2-19 fehlen, nicht kovalent gebunden war. Ob der Chromophor überhaupt jemals kovalent verknüpft wurde oder ob der Chromophor nur reversibel gebunden wird, sind Fragen, die ebenso wie die Frage weshalb der Chromophor in allen Phytochromen kovalent verknüpft ist in weiterführenden Studien untersucht werden sollen.

Ppr ist ein Hybrid von zwei Photorezeptoren, dem PYP („photoactive yellow protein“), und einem Bakteriophytochrom, gefolgt von einer Histidinkinase-Domäne (HK). Die beiden photochromen Domänen bilden mit den Chromophoren p-Hydroxyzimtsäure und BV die von anderen PYPs und Bakteriellen Phytochromen bekannten spektralen Eigenschaften aus. Das Spektrum des Holo-Holo-Ppr setzt sich dabei aus diesen Banden zusammen. Anders als bei anderen Phytochromen kann der im Dunkeln mit BV gebildete P_r Zustand der Phytochrom-Domäne durch rotes Licht nicht in den P_{fr} Zustand überführt werden. Stattdessen kommt es wie bei anderen Defektmutanten, u.a. der H250A Mutante von Agp1, nur zur Bleichung der Q-Bande. Die beobachtete Kinetik und die gefundene Protonenabgabe sprechen dafür, dass das Photoprodukt wie das der H250A Mutante von Agp1 Meta-R_C ähnlich ist.

Beleuchtung mit blauem Licht führt zur Bleichung der PYP-Domäne, wie sie auch bei anderen PYPs beobachtet wird und es bildet sich ein I_2 oder I_2' Intermediat. Der gebildete gebleichte Zustand hat im Gegensatz zu anderen PYPs eine Lebensdauer von mehreren Tagen. Die Ursache für die große Lebensdauer ist wahrscheinlich ein struktureller Unterschied im Bereich der Aminosäure M100. Der langlebige gebleichte Zustand der PYP-Domäne beeinflusst die spektroskopischen Eigenschaften der Phytochrom-Domäne. Unter anderem lässt sich die Phytochrom-Domäne bei gebleichter PYP-Domäne nicht mehr so stark bleichen, wie bei regenerierter PYP-Domäne. Der gebleichte Zustand der PYP-Domäne wiederum konnte durch violettes Licht (UV) wieder in den Dunkelzustand überführt werden, womit gleichzeitig auch die Beeinflussung der Phytochrom-Domäne aufgehoben wird. Die hier gefundenen spektralen Abhängigkeiten der beiden photochromen Domänen sind wahrscheinlich auf eine direkte Interaktion der beiden photochromen Domänen miteinander zurückzuführen und wären in dieser Form einmalig. Bei nachfolgenden Arbeiten geht es darum die gefundenen Abhängigkeiten zu bestätigen und genauer zu charakterisieren. Vor allem gilt es zu überprüfen, wie sich die verschiedenen Lichteinflüsse auf die Regulation der Polyketid-Synthase übertragen lassen, deren Expression durch Ppr reguliert wird.

Abstract

Phytochromes are photoreceptors first found in plants and recently also in cyanobacteria, fungi, algae and nonphotosynthetic bacteria.

Phytochromes switch between two spectrally distinct stable forms, the red- and far-red-light absorbing forms, denoted P_r and P_{fr}. The primary photochemical event for the P_r/P_{fr} photoconversion is the Z/E isomerization of the 15,16 double bond between rings C and D of the bilin chromophore.

All possible locked stereo isomers of the C/D-methine bridge are used to determinate the stereochemistry of the C/D methine bridge of BV in Agp1 from Agrobacterium tumefaciens. It could be shown that the chromophore has the 15Za geometry in P_r and 15Ea in P_{fr} excluding other configuration and conformation changes of this methine bridge during the photoconversion. The strong fluorescence of the 15Za adduct and the absence of transient absorption changes demonstrates that the Z/E-isomerization is blocked by the locked C/D methine bridge.

Density functional theory (DFT) proposed that the P_r/P_{fr}-photoconversion is accompanied by a change of the stereochemistry of the A/B methine bridge. Studies with the adduct of the 5Zs chromophore of Agp1, where the A/B methine bridge is locked in the 5Zs configuration, confirmed this prediction and showed that these changes taking place during the meta-R_A to meta-R_C transition. Thus another key step in the P_r/P_{fr}-photoconversion could be identified.

CD-spectroscopy in the visible region provides important information about the chirality of the chromophore. Comparisons of CD-spectra from different phytochromes and different biline adducts of Agp1 demonstrate that the chromophor has the same chirality in the P_r state of all phytochromes. The chirality is determined by the conjugated π-system and its extent over the chromophore. Plant and cyanobacterial phytochromes, which use PΦB and PCB as natural chromophores, showed a sign reversal of the Q-Band in the CD-spectra during the P_r to P_{fr} conversion. One hypothesis of this work is, that the sign reversal is a consequence of the Z/E isomerization of the 15, 16 double bond. The BV adduct and the non-covalent PCB and PΦB adducts of Agp1 don't showed this sign reversal, but the rotational strength is nearly zero in the P_{fr}-state. This could be explained by an opposite chirality of the A/B methine bridge to the C/D methine bridge in the P_{fr} state, so that they compensated each other leading to a nearly zero CD-signal. The covalent bound PCB and PΦB chromophores from Agp1 don't showed this compensation, because ring A isn't part of the conjugated system. These hypotheses have to be confirmed with other BV binding phytochromes.

The light-dependent step of the P_r/P_{fr} photoconversion is followed by several thermal relaxations via several spectrally distinct intermediates that are accompanied by structural changes of the chromophore and the surrounding protein.

The kinetics of the P_r/P_{fr} photoconversion of the BV adduct from Agp1 was studied by flash spectroscopy. The kinetics of Agp1 is similar to that of plant phytochromes and the three identified intermediates are named Lumi-R, Meta-R_A and Meta-R_C according to the nomenclature for the intermediates of plant phytochromes.

The transient absorption studies of the 18EtBV adduct of Agp1 showed that the kinetics is decelerated by the C18 vinyl group of BV. Because no other spectral properties are changed by the substitution of the vinyl through the ethyl group the accelerated kinetics of the 18EtBV adduct is presumably an effect of the higher flexibility of the ethyl group and sould be observed in other phytochromes too. The identification of the amino acids of the binding pocket involved is the topic of further investigations. One potential candidate is Y166 whose substi-

tution by an alanin lead to a decelerated kinetics and two spectral transitions for the meta-R_C formation.

The pH-dependency of the meta-R_C and P_{fr} formation and the big isotope effect of the meta-R_A and meta-R_C formation provide evidence that the kinetic of the P_r/P_{fr} photoconversion includes several rate limiting proton transfers. From Resonance Raman measurements it was concluded that the chromophore is protonated in P_r and P_{fr} and deprotonated in meta-R_C. This finding fits very well with the proton release during the meta-R_C formation and the uptake during the P_{fr} formation. Because a similar protonation pattern was observed for Cph1 the coupling of transient chromophore deprotonation and proton release may play a crucial role for the structural changes in the final step of the P_f formation.

The crystal structures of DrBphP from Deinococcus radiodurans and RpBphP3 from Rhodopseudomonas palustris in the P_r state showed that the protonated chromophore is stabilized through several hydrogen bonds to amino acids of the binding pocket. Substitution of two of these amino acids, D197 and H250, which are strongly conserved, by alanin leads to pK lowering of the protonated chromophore in comparison to WT. Furthermore both mutants cannot form a P_{fr} state after red light illumination. The photoproduct of H250A showed some sonsensusses with the intermediate meta-R_C of the WT. For D197A it isn’t clear what the nature of the photoproduct is. The data showed, as expected from the degree of conservation of both amino acids, that both amino acids play an crucial role for the P_{fr} formation. For D197 it could be the coupling of the protonated chromophore to the PHY-domain.

As studies with the M20 fragment, which lack the PHY domain, showed the PHY-domain is essential for the P_{fr} formation. This is surprising since the PHY domain isn’t part of the binding pocket which surrounds the chromophore. The kinetics after excitation of the P_r state is different from that of WT. The photoproduct formed showed spectral properties of the meta-R_C intermediate, so that is assumed that the photoproduct is meta-R_C like. The exact role of the PHY domain is subject of further studies.

Agp1 formed also photochrome adducts with non-covalently bound chromophores as the BV adduct of the mutant C20A showed, where the covalent binding is blocked. The non-covalent adduct showed specific spectral differences to the covalent adduct. On the basis of these differences it was discovered that the chromophore of M15Δ18N, who lacked the amino acids 2-19, wasn’t covalently bound to the protein either. The question whether the chromophore was covalently linked to the protein or if the chromophor was only reversibly bound has to be investigated in further studies. It is also interesting to resolve why the chromophore in all natural phytochromes is covalently bound.

Ppr is a hybrid of two photoreceptor proteins, photoactive yellow protein (PYP) and bacteriophytochrome (Bph), followed by a third histidine kinase (HK) domain. Assembly with the chromophores p-hydroxycinnamic acid and biliverdin lead to the typical spectral properties of PYP and bacteriophytochromes. The spectrum from holo-holo-Ppr is a superposition of the PYP and bacteriophytochrome spectra. Unlike other phytochromes the bacteriophytochrome domain of Ppr is not able to form the P_{fr} state. Red light leads to a bleach of the phytochrome domain from Ppr as observed for other defect phytochromes for example the H250A mutant from Agp1. The kinetics and the observed proton release support the idea that a meta-R_C like intermediat like the photoproduct from the H250A mutant from Agp1 is formed.

Illumination with blue light bleached the PYP domain as observed for other PYPs and the formation of an $I_2/I_2^{'}$ intermediate can be observed. This state has unlike other PYP’s a lifetime of 2-3 days. The reason for this long lifetime is a structural difference in the region of M100. The long living bleached state of the PYP-domain influenced the spectral properties of the phytochrome domain. The bleach of the phytchrome domain is less with a bleached PYP domain than with an unbleached PYP domain. With UV light the bleached PYP domain can

be photoreversed, which also abolishes the effect on the photoconversion of the phytochrome domain. The spectral dependencies of the PYP and phytochrome domains of Ppr are probably the result of an interaction between these domains. Future studies have to confirm these results and have to characterize the interaction. Another interesting point is, whether the different light effects are transferable to the regulation of the polyketid synthase, whose expression is regulated by Ppr.

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