

Anhang

A.1 Relation zwischen prompter Fluoreszenz und Q_A -Redoxzustand

Um aus den experimentell bestimmten Fluoreszenzintensitäten (F , F_M und F_0) den Anteil der Photosysteme mit reduziertem Q_A zu bestimmen, muss der Anregungsenergie transfer zwischen benachbarten Photosystemen berücksichtigt werden (PSII-Konnektivität). Die PSII-Konnektivität ist die Ursache für den nichtlinearen Zusammenhang zwischen dem Anteil der geschlossenen PSII-Zentren (Q_A ist reduziert) und der Intensität der prompten Fluoreszenz. Nach [Paillotin 1976] (siehe auch [Dau 1994]) gilt:

$$F = F_0 + \frac{(1-p)[Q_A^-]}{(1-p[Q_A^-])}(F_M - F_0), \quad (\text{A.1})$$

wobei $[Q_A^-] = \frac{c_{Q_A^-}}{c_{PSII}}$ den Anteil der Photosysteme mit reduziertem Q_A bezeichnet. Der Konnektivitätsparameter p gibt die Wahrscheinlichkeit für den Anregungsenergie transfer von einem geschlossenen Zentrum zu einem anderen Zentrum an.

$$p = \Phi_V \cdot \Phi_C$$

mit

$$\begin{aligned} \Phi_V &= \frac{F_M - F_0}{F_M} \\ \Phi_C &= \frac{k_C}{(k_C + k_F F_M^{-1})} = \frac{k_C}{(k_C + k_M)} \\ p &= \frac{F_M - F_0}{F_M} \cdot \frac{k_C}{k_C + k_F F_M^{-1}}. \end{aligned} \quad (\text{A.2})$$

k_M ist die Ratenkonstante der Deaktivierung des angeregten Zustandes eines geschlossenen Zentrums und beinhaltet alle Deaktivierungsprozesse (einschließlich Fluoreszenz) mit Ausnahme des Anregungsenergie transfers, k_F die Fluoreszenzratenkonstante und k_C die Ratenkonstante für den Anregungsenergie transfer.

Aus Gleichung A.1 ergibt sich für den Anteil der Zentren mit reduziertem Q_A :

$$\begin{aligned} [Q_A^-] &= \frac{F - F_0}{(F_M - F_0) + p(F - F_M)} \\ &= \frac{F - F_0}{(1-p)(F_M - F_0) + p(F - F_0)}. \end{aligned} \quad (\text{A.3})$$

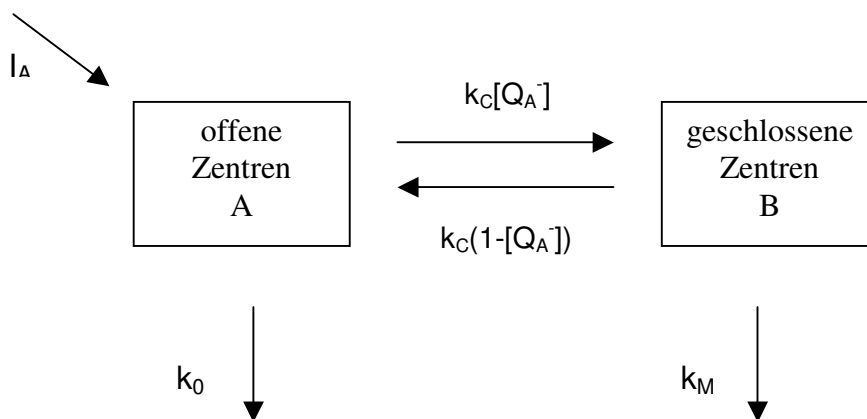
In dem Fall, dass keine Anregungsenergie zwischen den Photosystemen ausgetauscht wird ($p = 0$), gilt:

$$[Q_A^-] = \frac{F - F_0}{F_M - F_0} \quad (\text{A.4})$$

Für den Konnektivitätsparameter werden in der Literatur Werte zwischen 0,2 und 0,7 angegeben. Eine experimentelle Bestimmung ist z.B. über die Messung der Fluoreszenzinduktion möglich (siehe Kapitel 7).

A.2 Q_A^- -Korrektur der Rekombinationsfluoreszenz

Zur Ableitung des Zusammenhangs zwischen Rekombinationsfluoreszenz und Q_A -Redoxzustand wird folgendes Modell verwendet:



A, B: angeregte Photosysteme mit oxidiertem Q_A (offen) bzw. reduziertem Q_A (geschlossen)

I_A : durch Ladungsrekombination wiederangeregte Photosysteme pro Zeiteinheit

k_0, k_M : Rate der Deaktivierung des angeregten Zustandes A bzw. B (beinhaltet auch k_F , s. u.)

$[Q_A^-]$: Anteil der Photosysteme mit reduziertem Q_A

k_C : Rate des Anregungsenergie transfers zwischen Photosystemen

Die Ladungsrekombination führt zu einem angeregten Photosystem (A) mit oxidiertem Q_A (offenes Zentrum). Anregungsenergie transfer zwischen benachbarten Photosystemen ist möglich. Angeregte offene und geschlossene Zentren relaxieren strahlend oder strahlungslos oder transferieren die Anregungsenergie zu benachbarten Zentren.

Für den stationären Fall, d.h. die Repopulierung der Zustände A und B erfolgt mit der gleichen Geschwindigkeit wie die Deaktivierung, gelten dann die folgenden Ratengleichungen:

$$\frac{dA}{dt} = I_A - (k_0 + k_C)A + k_C(1 - [Q_A^-])B = 0$$

$$\frac{dB}{dt} = -(k_M + k_C(1 - [Q_A^-]))B + k_C[Q_A^-]A = 0$$

Berechnet wird jetzt die Zahl der angeregten Zentren A+B

$$B = \frac{k_C [Q_A^-]}{k_M + k_C (1 - [Q_A^-])} A$$

$$I_A = (k_0 + k_C [Q_A^-]) A - \frac{k_C^2 [Q_A^-] (1 - [Q_A^-])}{k_M + k_C (1 - [Q_A^-])} A = \frac{k_0 k_M + k_0 k_C (1 - [Q_A^-]) + k_M k_C [Q_A^-]}{k_M + k_C (1 - [Q_A^-])} A$$

$$\frac{A}{I_A} = \frac{k_M + k_C (1 - [Q_A^-])}{k_0 k_M + k_0 k_C + (k_M k_C - k_0 k_C) [Q_A^-]} = \frac{k_M + k_C (1 - [Q_A^-])}{k_0 (k_M + k_C) + k_C (k_M - k_0) [Q_A^-]}$$

$$\frac{A}{I_A} = \frac{\frac{1}{k_0} + (1 - [Q_A^-]) \frac{k_C}{k_M k_0}}{1 + \frac{k_C}{k_M k_0} [k_0 + (k_M - k_0) [Q_A^-]]}$$

$$A + B = A + \frac{k_C [Q_A^-]}{k_M + k_C (1 - [Q_A^-])} A = \frac{k_M + k_C (1 - [Q_A^-]) + k_C [Q_A^-]}{k_M + k_C (1 - [Q_A^-])} A$$

$$A + B = \frac{k_M + k_C}{k_0 k_M + k_0 k_C + (k_M k_C - k_0 k_C) [Q_A^-]} I_A$$

Die Zahl der angeregten Photosysteme ist:

$$A + B = \frac{\frac{1}{k_0} + \frac{k_C}{k_0 k_M}}{1 + \left[(1 - [Q_A^-]) k_0 + [Q_A^-] k_M \right] \frac{k_C}{k_0 k_M}} I_A$$

Spezialfälle:

Die Quantenausbeute der Fluoreszenzemission bezogen auf die Zahl der wiederangeregten Photosysteme lautet

$$\Phi_F^{del} = \frac{k_F (A + B)}{I_A},$$

wobei k_F die Ratenkonstante der Fluoreszenzemission ist. Damit gilt:

$$\Phi_F^{del} = k_F \frac{\frac{1}{k_0} + \frac{k_C}{k_0 k_M}}{1 + \left[(1 - [Q_A^-])k_0 + [Q_A^-]k_M \right] \frac{k_C}{k_0 k_M}}$$

Mit Hilfe der Quantenausbeute der prompten Fluoreszenz F_0 und F_M lassen sich k_0 und k_M eliminieren:

$$F_0 = \frac{k_F}{k_0}, \quad F_M = \frac{k_F}{k_M}$$

also

$$\Phi_F^{del} = \frac{F_0 + \frac{k_C}{k_F} F_0 F_M}{1 + \left[(1 - [Q_A^-]) \frac{k_F}{F_0} + [Q_A^-] \frac{k_F}{F_M} \right] \frac{k_C}{k_F^2} F_0 F_M}$$

und mit der Abkürzung $\bar{k}_C = \frac{k_C}{k_F}$ folgt

$$\begin{aligned} \Phi_F^{del} &= \frac{F_0 + \bar{k}_C F_0 F_M}{1 + \left[(1 - [Q_A^-]) F_M + [Q_A^-] F_0 \right] \bar{k}_C} = \frac{F_0 (1 + \bar{k}_C F_M)}{(1 + \bar{k}_C F_M) - \bar{k}_C (F_M - F_0) [Q_A^-]} \\ \Phi_F^{del} &= \frac{F_0 (1 + \bar{k}_C F_M - \bar{k}_C (F_M - F_0) [Q_A^-]) + F_0 \bar{k}_C (F_M - F_0) [Q_A^-]}{(1 + \bar{k}_C F_M) - \bar{k}_C (F_M - F_0) [Q_A^-]} \\ \Phi_F^{del} &= F_0 + \frac{F_0 \bar{k}_C [Q_A^-] (F_M - F_0)}{(1 + \bar{k}_C F_M) - \bar{k}_C (F_M - F_0) [Q_A^-]} \\ \Phi_F^{del} &= F_0 + \frac{F_0 \bar{k}_C [Q_A^-] \frac{F_M - F_0}{1 + \bar{k}_C F_M}}{1 - \frac{\bar{k}_C}{1 + \bar{k}_C F_M} (F_M - F_0) [Q_A^-]} \end{aligned}$$

Hier kann $\frac{(F_M - F_0) \bar{k}_C}{1 + \bar{k}_C F_M}$ durch den Konnektivitätsparameter p des Anregungsenergie transfers zwischen benachbarten Photosystemen ausgedrückt werden (siehe Gleichung A.2)

$$\begin{aligned} \frac{(F_M - F_0) \bar{k}_C}{1 + \bar{k}_C F_M} &= \frac{F_M - F_0}{F_M} \cdot \frac{\bar{k}_C}{F_M^{-1} + \bar{k}_C} = p \\ \frac{(F_M - F_0) \bar{k}_C}{1 + \bar{k}_C F_M} &= \Phi_V \cdot \frac{k_C}{k_F F_M^{-1} + k_C} = p \\ \frac{(F_M - F_0) \bar{k}_C}{1 + \bar{k}_C F_M} &= \Phi_V \cdot \Phi_C = p \end{aligned}$$

Damit folgt

$$\Phi_F^{del} = F_0 + \frac{p[Q_A^-]}{1-p[Q_A^-]} F_0.$$

Mit der Quantenausbeute für die Rekombination Φ_{rec} , die sich auf den Zustand bezieht, in dem Q_A in allen Zentren in reduzierter Form vorliegt ($[Q_A^-] = 1$), ergibt sich für die verzögerten Fluoreszenz:

$$F_{del} = \Phi_{rec}(t) \cdot \Phi_F^{del} \cdot [Q_A^-]$$

$$F_{del} = \Phi_{rec}(t) \left\{ F_0 + \frac{p[Q_A^-]}{1-p[Q_A^-]} F_0 \right\} \cdot [Q_A^-].$$

Mit

$$[Q_A^-] = \frac{F - F_0}{(1-p)(F_M - F_0) + p(F - F_0)} \quad (\text{Gl. A.3})$$

folgt

$$F_{del} = \Phi_{rec}(t) F_0 \left\{ 1 + \frac{p(F - F_0)}{(1-p)(F_M - F_0) + p(F - F_0) - p(F - F_0)} \right\} \cdot [Q_A^-]$$

$$F_{del} = \Phi_{rec}(t) \left\{ F_0 \frac{(1-p)(F_M - F_0) + p(F - F_0)}{(1-p)(F_M - F_0)} \right\} \cdot [Q_A^-].$$

Als Ergebnis erhält man:

$$F_{del} = \Phi_{rec}(t) F_0 \frac{F(t) - F_0}{(1-p)(F_M - F_0)} \quad (\text{A.5})$$

Die Abhängigkeit der verzögerten Fluoreszenz vom Q_A -Redoxzustand beschreibt der Quotient q

$$q = \frac{F(t) - F_0}{F_M - F_0}, \quad (\text{A.6})$$

der sich über die Messung des Zeitverlaufes der prompten Fluoreszenz nach Blitzanregung ermitteln lässt. Nach Division durch $(F - F_0)/(F_M - F_0)$ resultiert dann die Q_A^- -korrigierte Rekombinationsfluoreszenz, die nur noch von der $P680^+$ -Konzentration und der freien Energiedifferenz zum angeregten Antennenzustand abhängt.

A.3 Simulation der Fluoreszenz-Induktion

(Bestimmung der Absorptionsquerschnittes σ_{Abs} bzw. der Anregungsrate und des Konnektivitätsparameters p)

Unter der Annahme, dass

1. ein Anregungsenergietransfer zwischen Photosystemen möglich ist (PSII-Konnektivität)
2. es keine signifikanten Variationen in der PSII-Antennengröße gibt (keine PSII $_{\beta}$ -Units)
3. Rekombinations- oder sonstige Verlustprozesse vernachlässigbar sind

lässt sich der Anstieg der Fluoreszenzintensität, der durch die Zunahme der Photosysteme mit reduziertem Q_A verursacht wird, durch den folgenden rekursiven Ansatz beschreiben:

$$F(t + \Delta t) = F(t) + \frac{(1 - p)[Q_A^-(t + \Delta t)]}{1 - p[Q_A^-(t + \Delta t)]} (F_M - F_0)$$

mit der intensitätsabhängigen $[Q_A^-]$ -Zunahme

$$[Q_A^-(t + \Delta t)] = \left([Q_A^-(t)] + \left(\frac{F_M - F(t + \Delta t)}{F_M} \right) \Delta t \cdot \sigma_{\text{Abs}} \cdot I_A \right)$$

$(F_M - F)/F_M$:	Quantenausbeute der Q_A^- -Reduktion
F_M :	maximal erreichte Fluoreszenzintensität infolge der Belichtung
F_0 :	Fluoreszenzintensität im dunkeladaptierten Zustand
p :	Konnektivitätsparameter
σ_{Abs} :	Absorptionsquerschnitt PSII
I_A :	Photonenfluß in $1/(m^2s)$
Δt :	Zeitintervall zwischen zwei Datenpunkten
$[Q_A^-(t)]$:	Anteil oder relative Konzentration von reduziertem Q_A
$F(t)$:	Fluoreszenzintensität

Die Anpassung an die gemessene Induktionskurve erfolgte durch Minimierung der Summe der Fehlerquadrate unter Variation von σ_{Abs} , F_M , F_0 und p .

A.4 Geräte, Einstellungen und Steuerprotokolle

Geräte und Einstellungen des Rekombinationsfluoreszenz-Messplatzes

(Die Nummern beziehen sich auf die Beschriftungen in Abbildung 4.4.)

- (1) Laser: Minilite II Continuum, Blitzlampe und Q-Swich extern gesteuert durch (7)
- (2) Trigger-Photodiode
- (3) Delay-Generator – UN Gerätebau Pulsgenerator für Photomultiplier-Gating, Einstellungen: PM-Delay = 143 μ s, PM-Gatedauer = 3 μ s, Verzögerung („Messdelay“) = beliebig, Endpulsdauer = beliebig, Zyklenzahl = 000 (= externer Start). TTL-Belegung: Laser-Flashlamp-Ext → „ext.Start“, „PM-“ → Photomultiplier-„Gate“-Eingang
- (4) Hochspannungsnetzteil für HV1 – Heinzinger HNC 3000, U = -1000 V
- (5) Hochspannungsnetzteil für HV2 (Gegenspannung Gating) – Ltronix Power Supply 12,5K-10HR. U = -240 V
- (6) Oszilloskop – Tektronix 2445A (150 MHz) zur Verstärkung- und Offseteinkontrolle von Kanal 1 und 2
- (7) Steuergerät des „Double-Modulation Fluorometer FL 3000“ zur externen Lasersteuerung, AUX 4 = Laser-Flashlamp, AUX 6 = Q-Swich
- (8) Photomultiplier-Shutter, Compur Modell 1 156 006
- (9) Photomultiplier – R2066 HAMATSU mit Gating-Schaltsockel PMT Gated Socket Assembly C1392-55, Anodenwiderstand 2,2 k Ω
- (10) Filter 1: DT-Red (Linos Photonics)
- (11) Filter 2: DT-Magenta (Linos Photonics)
- (12) Vorverstärker für Kanal 1 – Preamp, Gain 30, BW 1,5 MHz, Input 1 M Ω
- (13) Verstärker 1 – Tektronix AM 502 mit Power Module TM 501 (Kanal 1), Gain 5, Bandbreite 100 kHz
- (14) Verstärker 2 – Tektronix AM 502 mit Power Module TM 501 (Kanal 2), Gain 2, Bandbreite 300 kHz
- (15) PC 1, Windows2000-Rechner mit PC-Messkarte PCI 9812, Ch 0 = Eingang Kanal 1, Ch 1 = Eingang Kanal 2, Ch 2 = Eingang Trigger-Photodiode
- (16) PC 2, Windows98-Rechner (Lasersteuerung)

Protokoll zur Lasersteuerung für die Messung der Rekombinationsfluoreszenz

(Programm der PC-Software des Steuermoduls des kinetischen Fluorometers)

```
; Version LN 27.1.99
MeasuringFlash=8us
MeasurDelay=3300ns
ActinicFlash=200ns
AuxDuration=ActinicFlash
PreFlash=10us
include default.inc ; Include standard options, don't remove it !
M_Voltage=20Num
F_Voltage=0Num
A_Voltage=F_Voltage
.*****
;vF-LASERSTEUERUNG
;
;PM-Gate Delay = QDelay - 6..7µs bei 3µs Gatepuls
;(entspricht 10µs PM-Totzeit)
;
QPeriod=700ms
NQ=32Num
FlashVorlauf=4*QPeriod
QDelay=150us
;
; A4 - Blitzlampe
; A6 - Q-Swich
;
; BLITZLAMPE-VORLAUF
k=<0ms,QPeriod..FlashVorlauf-QPeriod>
k=>A4(50us)
;
; Q-SWICH UND BLITZLAMPE
i=FlashVorlauf+<0ms,QPeriod..(NQ-1)*QPeriod>
j=FlashVorlauf+QDelay+<0,QPeriod..(NQ-1)*QPeriod>
i=>A4(50us)
j=>A6(2us)
```

Protokoll zur Lasersteuerung und Signaldetektion für die Messung der prompten Fluoreszenz

(Programm der PC-Software des Steuermoduls des kinetischen Fluorometers)

```
; S-States-Laser
; Version LN 27.1.99
MeasuringFlash=8us
MeasurDelay=3300ns
ActinicFlash=200ns
AuxDuration=ActinicFlash
PreFlash=10us
include default.inc ; Include standard options, don't remove it !
M_Voltage=20Num
F_Voltage=0Num
A_Voltage=F_Voltage
.*****
;pF-Lasersteuerung und Messung
```



```
;
QPeriod=700ms
NQ=32Num
FlashVorlauf=4*QPeriod
QDelay=150us
;
; A4 - Blitzlampe
; A6 - Q-Swich
;
; BLITZLAMPE-VORLAUF
<0ms,QPeriod..FlashVorlauf-QPeriod>=>A4(50us)
;
; Q-SWICH UND BLITZLAMPE
i=FlashVorlauf+<0ms,QPeriod..(NQ-1)*QPeriod>
j=FlashVorlauf+QDelay+<0,QPeriod..(NQ-1)*QPeriod>
i=>A4(50us)
j=>A6(2us)
;
; Fo MEASUREMENT
k=FlashVorlauf-1.2ms+<200us,400us..1000us>
k=>fm1
;
; REOXIDATION KINETICS
x=[76us,115us..QPeriod]
;x=[30us,47us..QPeriod]
y=FlashVorlauf+QDelay+<0,QPeriod..(NQ-2)*QPeriod>
y#x=>fm1
;
z=FlashVorlauf+(NQ-1)*QPeriod+QDelay+[76us,115us..72000ms]
z=>fm1
```

A.5 Pufferlösungen und Reagenzien

Puffer A (für Messungen bei pH 6,4)

25 mM MES (2-Morpholinoethanesulfonic acid, 99,5 %)
10 mM NaCl
5 mM MgCl₂
5 mM CaCl₂
1 M Glycin-Betain (Betain-monohydrat, 99 %)

Puffer B (für Messungen bei pH 4,5 - 8,5)

25 mM MES (2-Morpholinoethanesulfonic acid, 99,5 %)
25 mM MOPS (3-Morpholinopropanesulfonic acid, 99,5 %)
25 mM EPPS (4-(2-Hydroxyethyl)piperazine-1-propanesulfonic acid, 98 %)
10 mM NaCl
5 mM MgCl₂
5 mM CaCl₂
1 M Glycin-Betain (Betain-monohydrat, 99 %)

Der pH-Wert der Puffer wurde durch Zugabe von NaOH bzw. HCl eingestellt.

Elektronenakzeptoren

DCBQ 2,6-Dichloro-1,4-benzoquinone (98 %)
PPBQ Phenyl-p-benzoquinone (95 %)
Kalium-Hexacyanoferrat(III) (99 %)

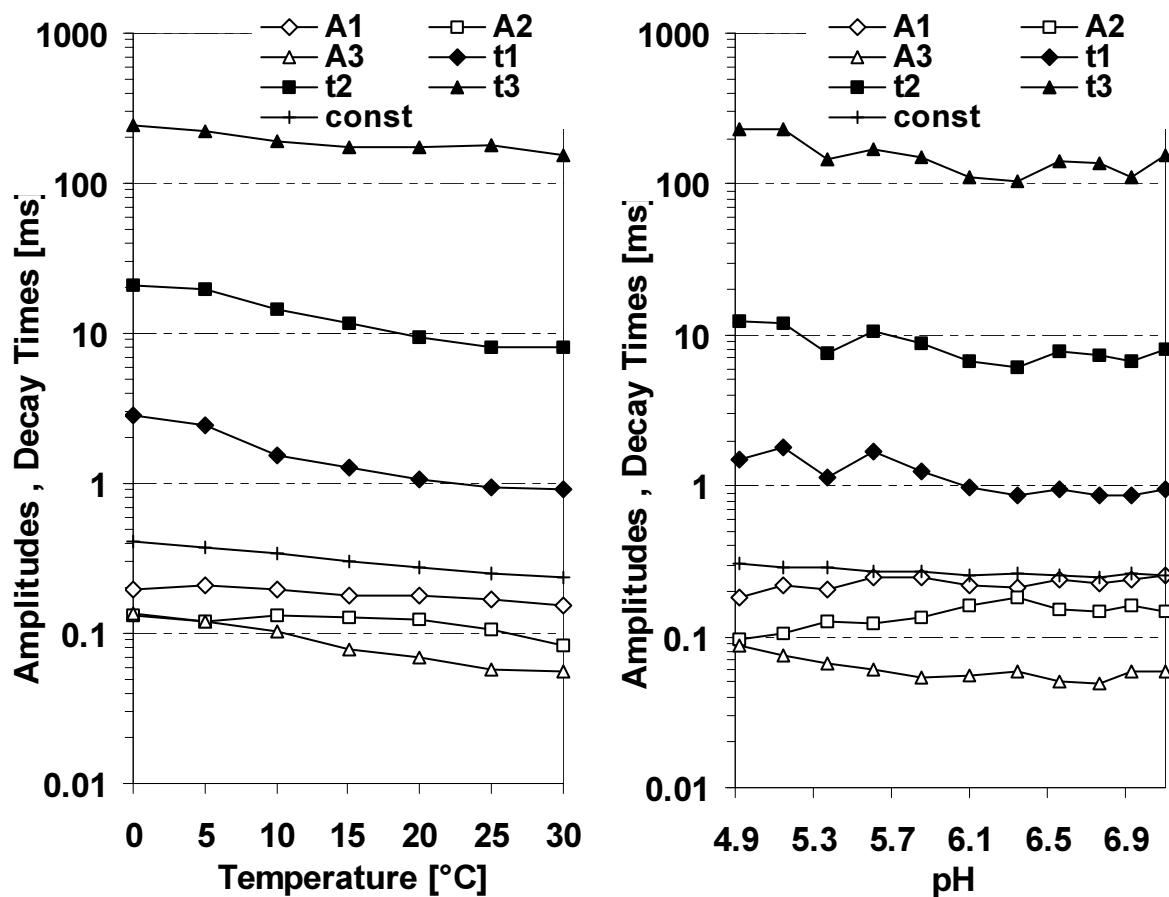
Lösungsmittel für die DCBQ und PPBQ: DMSO - Dimethylsulfoxid

Akzeptorseiten-Inhibitor

DCMU - 3-(3,4-Dichlorophenyl)-1,1-Dimethylurea (97 %)

A.6 Simulationsparameter der prompten Fluoreszenz

(Beispiel für die Simulationsparameter der prompten Fluoreszenz, die zur Generierung der Korrekturkurven für die Q_A^- -Korrektur der Rekombinationsfluoreszenz verwendet wurden.)



Dargestellt sind die Zeitkonstanten und Amplituden der 3fach-exponentiellen Beschreibung der Abfälle der prompten Fluoreszenz nach Anregung mit einem sättigenden Laserpuls für den dritten Blitz. Links: Temperaturabhängigkeit bei pH 6,4, rechts: pH-Abhängigkeit bei 20 °C.

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