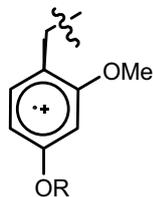# Electron Transfer in Peptides: The Influence of Charged Amino Acids**

*Jian Gao, Pavel Müller, Min Wang, Sonja Eckhardt, Miriam Lauz, Katharina M. Fromm, and Bernd Giese**

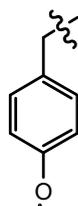# 1. Abbreviations

EA$^{\bullet+}$ (**e**lectron **a**cceptor):

ED$^{\bullet}$ (oxidated, deprotonated **e**lectron **d**onor):

RA$^{\bullet+}$ (oxidated **r**elay **a**mino acid):
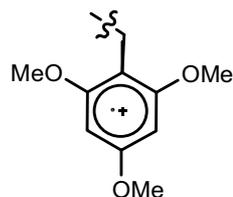
2. Precursors of the electron acceptor

Precursor of 2a and 2b:
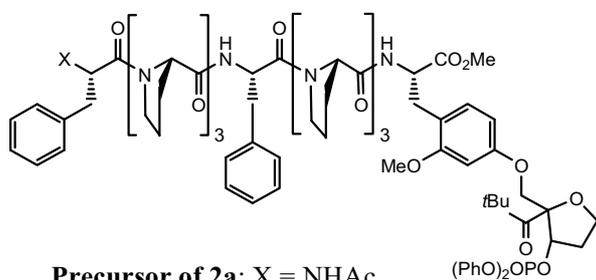
Precursor of 2a: X = NHAc

Precursor of 2b: X = $\overset{\oplus}{N}H_3$ $CF_3CO_2^{\ominus}$

Precursor of 4:
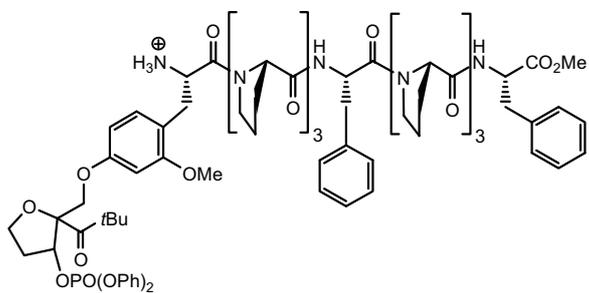
Precursor of 10a and 10b:
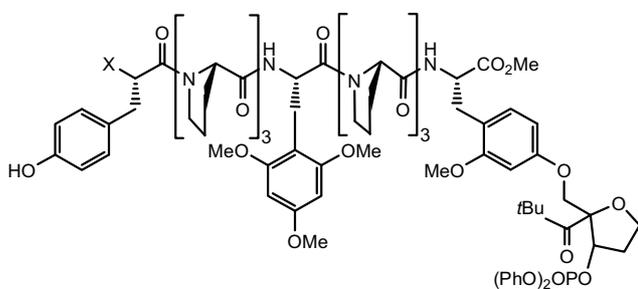
precursor of 10a: X = NHAc
precursor of 10b: X = $\overset{\oplus}{N}H_3$ $CF_3CO_2^{\ominus}$

Precursor of 11a and 11b:
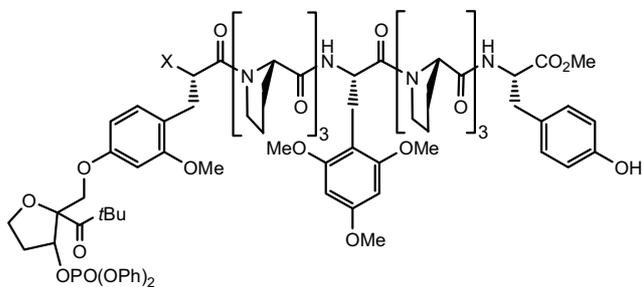
precursor of 11a: X = NHAc
precursor of 11b: X = $\overset{\oplus}{N}H_3$ $CF_3CO_2^{\ominus}$

2. Setup for laser experiments
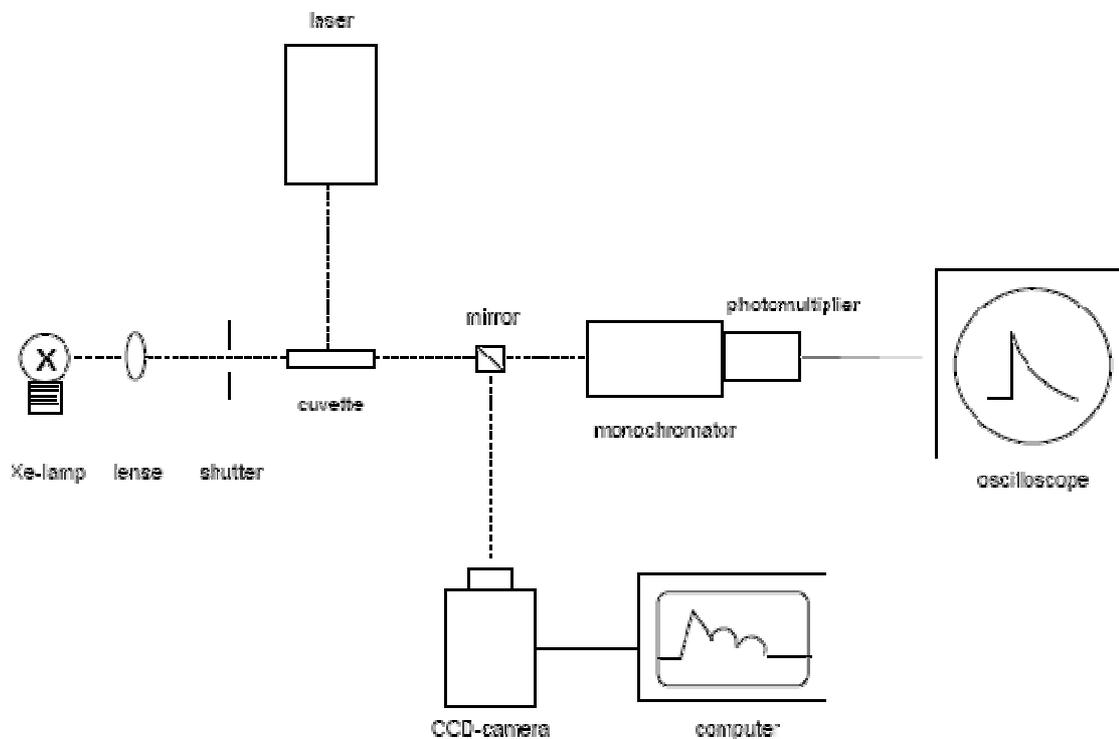
For the generation of the radical cation ($EA^{\bullet+}$) a XeCl-excimer laser with a wavelength of 308 nm and an energy of 100-130 mJ was used. It was directed to a UV-cuvette, which allowed for degassing and storing the sample under vacuum. Orthogonal to the laser a pulsed Xe-lamp was installed in order to measure the transient UV-spectra. For recording the UV-spectra between 400 and 600 nm after a defined time delay a fast electronic shutter and a CCD-camera were used.

3. INTERMOLECULAR E.T.

3.1 Precursor of 2a and 3a: 5.0 mM solution in CH₃CN/H₂O 3:1, 1:1 ratio, 20 °C
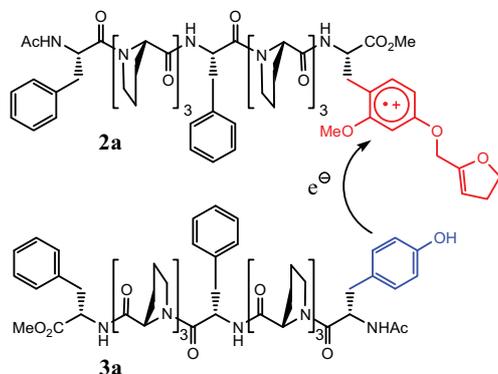
Time (ns)	EA$^{\bullet+}$	ED$^{\bullet}$
40	0.924	0.076
100	0.709	0.291
150	0.617	0.383
200	0.578	0.422
250	0.546	0.454
300	0.508	0.492
1000	0.378	0.622

Output from Specfit

[PROGRAM]
Name = SPECFIT VB5
Version = 3.0

[MODEL]
Date = 22-Jan-10
Time = 13:31:24
Model = 2
Index = 4
Function = 2
Species = 2
Params = 1

[TYPE]
Pseudo-First Order, A -> B

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1.000E+00	True	True	INJ.FIX
B	0.000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	2.24503E+06 +/-	2.97521E+05	/sec

[TIME ZERO]

Tzero = 4E-08

[CONVERGENCE]
Iters = 3
Convergence = 1.000E-03
MarqConv = 1.529E-15
MarqPar = 0.0
SqSumY = 1.815E-01
SigmaY = 1.136E-02

[COVARIANCE]
8.852E+10

[CORRELATION]
1.000E+00

[END FILE]

3.2 Precursor of 2b and 3b: 5.0 mM solution in CH$_3$CN/H$_2$O 3:1, 1:1 ratio, 20 °C
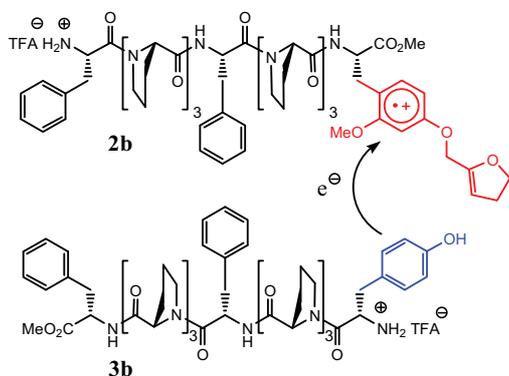
Time (ns)	EA$^{\bullet+}$	ED$^\bullet$
40	0.995	0.005
300	0.770	0.230
1000	0.499	0.501

Output from Specfit

[PROGRAM]
Name = SPECFIT VB5
Version = 3.0

[MODEL]
Date = 22-Jan-10
Time = 12:39:34
Model = 2
Index = 4
Function = 2
Species = 2
Params = 1

[TYPE]
Pseudo-First Order, A -> B

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1.000E+00	True	True	INJ.FIX
B	0.000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	7.26794E+05 +/-	4.02370E+04	/sec

[TIME ZERO]
Tzero = 4E-08

[CONVERGENCE]
Iters = 3
Convergence = 1.000E-03
MarqConv = -1.933E-15
MarqPar = 0.0
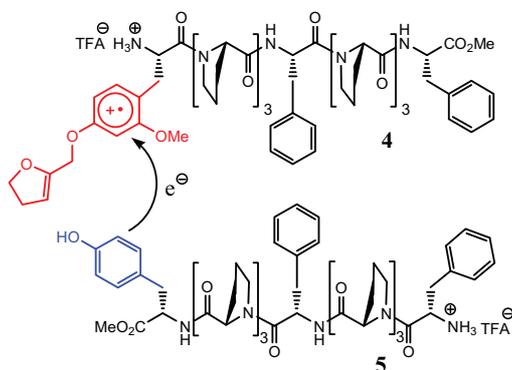SqSumY = 3.589E-03
SigmaY = 2.442E-03

[COVARIANCE]
1.619E+09

[CORRELATION]
1.000E+00

[END FILE]

3.3 Precursor of 4 and 5: 1.0 mM solution in CH$_3$CN/H$_2$O 3:1, 1:1 ratio, 20 °C

Time (ns)	EA$^{\bullet+}$	ED$^{\bullet}$
40	0.778	0.222
100	0.767	0.234
200	0.604	0.396
500	0.504	0.496

Output from Specfit

[PROGRAM]
Name = SPECFIT VB5
Version = 3.0

[MODEL]
Date = 22-Jan-10
Time = 14:23:23
Model = 2
Index = 4
Function = 2
Species = 2
Params = 1

[TYPE]
Pseudo-First Order, A -> B

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1.000E+00	True	True	INJ.FIX
B	0.000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	1.87839E+06 +/-	3.42381E+05	/sec

[TIME ZERO]
Tzero = 4E-08

[CONVERGENCE]
Iters = 3
Convergence = 1.000E-03
MarqConv = 1.759E-15
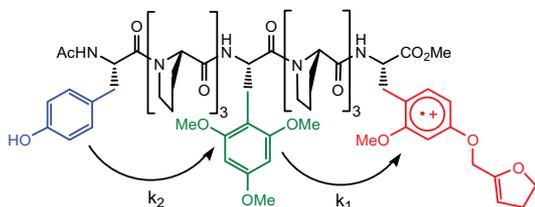
MarqPar = 0.0
SqSumY = 8.678E-02
SigmaY = 1.040E-02

[COVARIANCE]
1.172E+11

[CORRELATION]
1.000E+00

[END FILE]

4. INTRAMOLECULAR E.T.

4.1 Precursor of 10a: 5.0 mM solution in CH$_3$CN/H$_2$O 3:1, 20 °C

Time (ns)	EA$^{\bullet+}$	RA$^{\bullet+}$	ED$^{\bullet}$
40	0.513	0.155	0.332
60	0.486	0.118	0.396
100	0.419	0.099	0.482
150	0.384	0.071	0.545
200	0.363	0.036	0.601
300	0.340	0.047	0.613
400	0.326	0.018	0.656
500	0.325	0.019	0.656

Output from Specfit
[PROGRAM]
Name = SPECFIT110VB6
Version = 3.0

[MODEL]
Date = 25. Feb. 10
Time = 11:29:43
Model = 2
Index = 4
Function = 5
Species = 3
Params = 2

[TYPE]
2 Exponentials, A -> B -> C

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1,000E+00	Wahr	Wahr	INJ.FIX
B	0,000E+00	Wahr	Wahr	TMP.FIX
C	0,000E+00	Wahr	Wahr	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]		[ERROR]	[UNITS]
k1	False	5,48112E+06	+/-	8,67059E+05	/sec
k2	False	3,07188E+07	+/-	1,45545E+07	/sec

[TIME ZERO]
Tzero = 4E-08

[CONVERGENCE]
Iters = 19
Convergence = 1,000E-03
MarqConv = 3,952E-04

MarqPar = 0,0
SqSumY = 6,289E-01
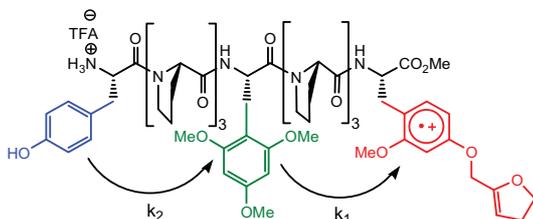SigmaY = 1,978E-02

[COVARIANCE]
7,518E+11   -1,245E+12
-1,245E+12   2,118E+14

[CORRELATION]
1,000E+00   -9,866E-02
-9,866E-02   1,000E+00

[END FILE]

4.2 Precursor of 10b: 5.0 mM solution in CH₃CN/H₂O 3:1, 20 °C

Time (ns)	EA⁺	RA⁺	ED
40	0.811	0.189	0.000
80	0.757	0.188	0.055
100	0.652	0.188	0.160
150	0.670	0.162	0.168
200	0.506	0.144	0.350
500	0.433	0.146	0.421

Output from Specfit

[PROGRAM]
Name = SPECFIT110VB6
Version = 3.0

[MODEL]
Date = 06. Apr. 10
Time = 14:37:08
Model = 2
Index = 4
Function = 5
Species = 3
Params = 2

[TYPE]
2 Exponentials, A -> B -> C

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1,000E+00	True	True	INJ.FIX
B	0,000E+00	True	True	TMP.FIX
C	0,000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	2,71542E+06 +/-	3,21516E+05	/sec
k2	False	7,72557E+06 +/-	1,95426E+06	/sec

[TIME ZERO]
Tzero = 4E-08

[CONVERGENCE]
Iters = 3
Convergence = 1,000E-03
MarqConv = 8,016E-14
MarqPar = 0,0
SqSumY = 1,575E-01
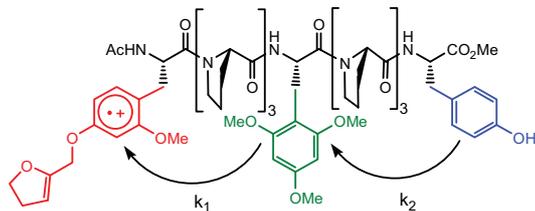SigmaY = 1,143E-02

[COVARIANCE]
1,034E+11   7,932E+10
7,932E+10   3,819E+12

[CORRELATION]
1,000E+00   1,262E-01
1,262E-01 1,000E+00

[END FILE]

4.3 Precursor of 11a: 2.0 mM solution in CH_3CN/H_2O 3:1, 20 °C

Time (ns)	$EA^{•+}$	$RA^{•+}$	$ED^•$
40	0.806	0.008	0.185
60	0.753	0.015	0.232
80	0.757	0.008	0.235
100	0.677	0.001	0.322
250	0.548	0.001	0.452
500	0.449	0.012	0.539

Output from Specfit
[PROGRAM]
Name = SPECFIT110VB6
Version = 3.0

[MODEL]
Date = 06. Apr. 10
Time = 14:41:02
Model = 2
Index = 4
Function = 5
Species = 3
Params = 2

[TYPE]
2 Exponentials, A -> B -> C

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1,000E+00	True	True	INJ.FIX
B	0,000E+00	True	True	TMP.FIX
C	0,000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	2,35308E+06 +/-	2,73227E+05	/sec

k2 >>k1; k2 cannot be determined

[TIME ZERO]
Tzero = 4E-08

[CONVERGENCE]
Iters = 3
Convergence = 1,000E-03
MarqConv = 2,218E-13
MarqPar = 0,0
SqSumY = 1,164E-01
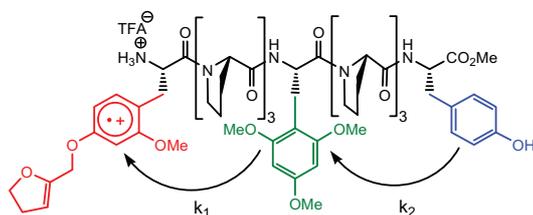SigmaY = 9,827E-03

[COVARIANCE]
7,465E+10   -1,197E+35
-1,197E+35   4,103E+60

[CORRELATION]
1,000E+00   -2,162E-01
-2,162E-01   1,000E+00

[END FILE]

4.4 Precursor of 11b: 1.0 mM solution in CH$_3$CN/H$_2$O 3:1, 20 °C

Time (ns)	EA$^{\bullet+}$	RA$^{\bullet+}$	ED$^{\bullet}$
30	0.568	0.000	0.432
40	0.502	0.009	0.489
60	0.424	0.003	0.573

Output from Specfit
[PROGRAM]
Name = SPECFIT110VB6
Version = 3.0

[MODEL]
Date = 06. Apr. 10
Time = 14:43:18
Model = 2
Index = 4
Function = 5
Species = 3
Params = 2

[TYPE]
2 Exponentials, A -> B -> C

[SPECIES]	[INIT.CONC]	[COLORED]	[FIXED]	[SPECTRUM]
A	1,000E+00	True	True	INJ.FIX
B	0,000E+00	True	True	TMP.FIX
C	0,000E+00	True	True	TYR.FIX

[NAME]	[FIXED]	[PARAMETER]	[ERROR]	[UNITS]
k1	False	1,63575E+07 +/-	8,28789E+05	/sec

k2 >>k1; k2 cannot be determined

[TIME ZERO]
Tzero = 3E-08

[CONVERGENCE]
Iters = 3
Convergence = 1,000E-03
MarqConv = 0,000E+00
MarqPar = 0,0
SqSumY = 9,130E-03
SigmaY = 3,894E-03

[COVARIANCE]
6,869E+11   -1,827E+16

-1,827E+16   6,109E+21

[CORRELATION]
1,000E+00   -2,820E-01
-2,820E-01   1,000E+00

[END FILE]

5. CD-spectroscopy

5.1 CD-spectra of precursors of 11a (black) and 11b (red)