Photoexcitation dynamics of p-nitroaniline and *N,N*-dimethyl-p-nitroaniline in 1-alkyl-3-methylimidazolium-cation based ionic liquids with different alkyl chain lengths

Yoshifumi Kimura*, Shinya Ibaraki, Ryusei Hirano, Yosuke Sugita, Yoshiro Yasaka, Masakatsu Ueno

Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe, Kyoto, 610-0321, Japan

Corresponding Author

Y. Kimura

Email: yokimura@mail.doshisha.ac.jp

Tel: +81-774-65-6561

FAX: +81-774-65-6801

Table S1. Relative amplitudes and time constants obtained by the coevolution fit of the transient absorption profiles of pNA at different probe wavelengths to the multi-exponential function. The value of τ_3 is fixed to be 1000 ps. The errors are estimated from the residual of the fit and correlations of error matrix for each transient.

365 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.04	-1.01 ± 0.03	-0.11 ± 0.01	1.5 ± 0.1	7.4 ± 0.2
C_4mim^+	-1± 0.06	-0.97 ± 0.04	-0.11 ±0.01	1.7 ± 0.1	8.0 ± 0.3
C_6mim^+	-1 ± 0.04	-1.19 ± 0.04	-0.17 ± 0.01	1.5 ± 0.1	7.9 ± 0.3
C_8mim^+	-1 ± 0.05	-1.00 ± 0.05	-0.15 ± 0.01	2.0 ± 0.1	8.1 ± 0.3
$C_{10}mim^+$	-1 ± 0.03	-1.41 ± 0.03	-0.20 ± 0.01	1.6 ± 0.1	7.5 ± 0.2
$C_{12}mim^+$	-1 ± 0.09	-1.45 ± 0.07	-0.22 ± 0.01	1.6 ± 0.2	7.5 ± 0.4

380 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.04	-0.51 ± 0.04	-0.017 ±0.005	1.7 ± 0.1	8.6 ± 0.7
C_4mim^+	-1 ± 0.04	-0.56 ± 0.04	-0.027 ± 0.005	1.7 ± 0.1	8.5 ± 0.6
C_6mim^+	-1 ± 0.05	-0.62 ± 0.05	-0.038 ± 0.005	1.9 ± 0.1	8.4 ± 0.7
C_8mim^+	-1 ± 0.05	-0.62 ± 0.05	-0.045 ± 0.005	1.9 ± 0.1	8.3 ± 0.6
$C_{10}mim^+$	-1 ± 0.05	-0.65 ± 0.06	-0.059 ± 0.005	2.0 ± 0.1	8.7 ± 0.7
$C_{12}mim^+$	-1 ± 0.05	-0.77 ± 0.06	-0.077 ± 0.005	2.0 ± 0.1	8.7 ± 0.6

420 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.44 ± 0.01	0.051 ± 0.001	0.38 ± 0.01	2.7 ± 0.1
C_4mim^+	-1± 0.01	0.41 ± 0.01	0.047 ± 0.001	0.48 ± 0.01	2.8 ± 0.1
C_6mim^+	-1 ± 0.01	0.41 ± 0.01	0.053 ± 0.001	0.41 ± 0.01	3.1 ± 0.1
C_8mim^+	-1 ± 0.01	0.43 ± 0.01	0.046 ± 0.001	0.55 ± 0.01	3.2 ± 0.1
$C_{10}mim^+$	-1 ± 0.01	0.40 ± 0.01	0.049 ± 0.001	0.46 ± 0.01	3.4 ± 0.1
$C_{12}mim^+$	-1 ± 0.01	0.40 ± 0.01	0.041 ± 0.001	0.37 ± 0.02	3.2 ± 0.1

440 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.55 ± 0.01	0.049 ± 0.001	0.55 ± 0.01	4.2 ± 0.1
C_4mim^+	-1± 0.01	0.57 ± 0.01	0.047 ± 0.001	0.57 ± 0.01	4.6 ± 0.1
C_6mim^+	-1 ± 0.01	0.56 ± 0.01	0.052 ± 0.001	0.56 ± 0.01	4.9 ± 0.1
C_8mim^+	-1 ± 0.01	0.56 ± 0.01	0.054 ± 0.001	0.56 ± 0.01	5.4 ± 0.1
$C_{10}mim^+$	-1 ± 0.01	0.52 ± 0.01	0.051 ± 0.001	0.52 ± 0.01	5.1 ± 0.1
$C_{12}mim^+$	-1 ± 0.01	0.53 ± 0.01	0.068 ± 0.001	0.53 ± 0.01	5.2 ± 0.1

458 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.40 ± 0.01	0.051 ± 0.001	0.38 ± 0.01	2.7 ± 0.1
C_4mim^+	-1± 0.01	0.44 ± 0.01	0.047 ± 0.001	0.48 ± 0.01	2.8 ± 0.1
C_6mim^+	-1 ± 0.01	0.39 ± 0.01	0.053 ± 0.001	0.41 ± 0.01	3.1 ± 0.1
C_8mim^+	-1 ± 0.01	0.44 ± 0.01	0.046 ± 0.001	0.55 ± 0.01	3.2 ± 0.1
$C_{10}mim^+$	-1 ± 0.01	0.37 ± 0.01	0.049 ± 0.001	0.46 ± 0.01	3.4 ± 0.1
$C_{12}mim^+$	-1 ± 0.01	0.29 ± 0.01	0.041 ± 0.001	0.36 ± 0.01	3.2 ± 0.1

474 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.41 ± 0.02	0.077 ± 0.001	0.34 ± 0.01	2.0 ± 0.1
C_4mim^+	-1± 0.01	0.45 ± 0.02	0.068 ± 0.001	0.40 ± 0.01	2.1 ± 0.1
C_6mim^+	-1 ± 0.01	0.41 ± 0.01	0.075 ± 0.001	0.39 ± 0.01	2.2 ± 0.1
C_8mim^+	-1 ± 0.01	0.36 ± 0.01	0.078 ± 0.001	0.40 ± 0.01	2.6 ± 0.1
$C_{10}mim^+$	-1 ± 0.01	0.39 ± 0.01	0.082 ± 0.001	0.38 ± 0.01	2.6 ± 0.1
$C_{12}mim^+$	-1 ± 0.01	0.33 ± 0.01	0.067 ± 0.001	0.30 ± 0.01	2.3 ± 0.1

Table S2. Relative amplitudes and time constants obtained by the coevolution fit of the transient absorption profiles of DMpNA at different probe wavelengths to the multi-exponential function. The value of τ_3 is fixed to be 1000 ps. The errors are estimated from the residual of the fit and correlations of error matrix for each transient.

365 nm

Cation	A_0	A_1	A_2	A_3	τ_0	τ_1	τ_2
C_2mim^+	0.39 ± 0.29	-1 ± 0.45	-0.40 ± 0.03	-0.054 ± 0.001	0.68 ± 0.01	3.2 ± 0.1	10.8 ± 0.1
C_4mim^+	0.36 ± 0.03	-1± 0.04	-0.37 ± 0.04	-0.052 ±0.002	0.60 ± 0.09	2.8 ± 0.2	9.1 ± 0.9
C_6mim^+	0.71 ± 0.38	-1 ± 0.26	-0.80 ± 0.04	-0.089 ± 0.003	1.0 ± 0.3	2.7 ± 0.9	8.4 ± 1.0
C_8mim^+	0.91 ± 0.52	-1 ± 0.31	-1.36 ± 0.05	-0.21 ± 0.01	0.93 ± 0.34	2.6 ± 1.5	8.0 ± 1.0
$C_{10}mim^+$	0.92 ± 1.01	-1 ± 0.89	-0.92 ± 0.03	-0.14 ± 0.01	1.1 ± 0.5	2.2 ± 1.2	8.4 ± 0.8
$C_{12}mim^+$	1.1 ± 0.96	-1 ± 0.84	-1.08 ± 0.07	-0.15 ± 0.01	1.1 ± 0.4	2.2 ± 1.1	7.7 ± 0.5

380 nm

Cation	A_0	A_1	A_2	A_3	τ_0	τ_1	τ_2
C_2mim^+	1.54 ± 3.15	-1 ± 0.30	-0.50 ± 0.08	-0.032 ± 0.003	0.27 ± 0.02	1.9 ± 0.2	7.6 ± 0.7
C_4mim^+	1.39 ± 3.78	-1± 0.32	-0.35 ± 0.05	-0.032 ±0.002	0.24 ± 0.02	2.1 ± 0.1	8.2 ± 0.6
C_6mim^+	1.64 ± 5.84	-1 ± 0.34	-0.59 ± 0.09	-0.061± 0.003	0.25 ± 0.18	2.7 ± 0.2	8.5 ± 0.7
C_8mim^+	1.78 ± 6.02	-1 ± 0.37	-0.70 ± 0.12	-0.084 ± 0.003	0.29 ± 0.02	2.7 ± 0.2	8.0 ± 0.6
$C_{10}mim^+$	1.81 ± 1.56	-1 ± 0.16	-0.75 ± 0.14	-0.094 ± 0.002	0.28 ± 0.01	3.0 ± 0.3	7.8 ± 0.7
$C_{12}mim^+$	1.77 ± 1.51	-1 ± 0.17	-0.72 ± 0.15	-0.095± 0.002	0.27 ± 0.01	3.2 ± 0.3	8.0 ± 0.8

405 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.02	-0.01 ± 0.02	-0.011 ± 0.003	2.3 ± 0.1	12.7 ± 3.3
C_4mim^+	-1± 0.02	-0.07 ± 0.02	-0.011 ±0.003	2.7 ± 0.1	13.3 ± 4.3
C_6mim^+	-1 ± 0.03	-0.10 ± 0.03	-0.010± 0.004	2.8 ± 0.1	13.2 ± 3.8
C_8mim^+	-1 ± 0.06	-0.15 ± 0.07	-0.009 ± 0.004	2.7 ± 0.2	9.9 ± 3.3
$C_{10}mim^+$	-1 ± 0.04	-0.08 ± 0.04	-0.019 ± 0.003	3.1 ± 0.1	12.0 ± 5.1
$C_{12}mim^+$	-1 ± 0.03	-0.05 ± 0.03	-0.019± 0.003	3.3 ± 0.1	13.3 ± 7.4

420 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.04	0.09 ± 0.04	0.003 ± 0.002	1.9 ± 0.1	5.2 ± 0.1
C_4mim^+	-1± 0.04	0.12 ± 0.04	0.007 ± 0.002	2.1 ± 0.1	5.6 ± 0.1
C_6mim^+	-1 ± 0.01	0.11 ± 0.01	0.006 ± 0.001	2.2 ± 0.1	6.3 ± 0.1
C_8mim^+	-1 ± 0.01	0.10 ± 0.01	0.005 ± 0.001	2.3 ± 0.1	6.9 ± 0.2
$C_{10}mim^+$	-1 ± 0.01	0.11 ± 0.01	0.009 ± 0.001	2.3 ± 0.1	6.8 ± 0.2
$C_{12}mim^+$	-1 ± 0.01	0.12 ± 0.01	0.015 ± 0.001	2.4 ± 0.1	6.6 ± 0.2

440 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.04	0.39 ± 0.01	0.017 ± 0.001	1.2 ± 0.1	7.4 ± 0.2
C_4mim^+	-1± 0.04	0.38 ± 0.01	0.024 ± 0.002	1.2 ± 0.1	8.2 ± 0.3
C_6mim^+	-1 ± 0.01	0.40 ± 0.01	0.031 ± 0.001	1.3 ± 0.1	8.1 ± 0.2
C_8mim^+	-1 ± 0.01	0.40 ± 0.01	0.035 ± 0.002	1.4 ± 0.1	8.3 ± 0.3
$C_{10}mim^+$	-1 ± 0.01	0.39 ± 0.01	0.038 ± 0.002	1.3 ± 0.1	8.7 ± 0.4
$C_{12}mim^+$	-1 ± 0.02	0.40 ± 0.02	0.044 ± 0.003	1.3 ± 0.1	8.8 ± 0.6

458 nm

Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.42 ± 0.01	0.015 ± 0.001	0.78 ± 0.01	5.2 ± 0.1
C_4mim^+	-1± 0.01	0.43 ± 0.01	0.023 ± 0.001	0.84 ± 0.01	5.6 ± 0.1
C_6mim^+	-1 ± 0.01	0.40 ± 0.01	0.031 ± 0.001	0.85 ± 0.01	6.3 ± 0.1
C_8mim^+	-1 ± 0.01	0.43 ± 0.04	0.022 ± 0.001	1.17 ± 0.03	6.9 ± 0.2
$C_{10}mim^+$	-1 ± 0.01	0.38 ± 0.01	0.039 ± 0.001	0.92 ± 0.02	6.8 ± 0.2
$C_{12}mim^+$	-1 ± 0.01	0.37 ± 0.01	0.044 ± 0.001	0.96 ± 0.02	6.6 ± 0.2

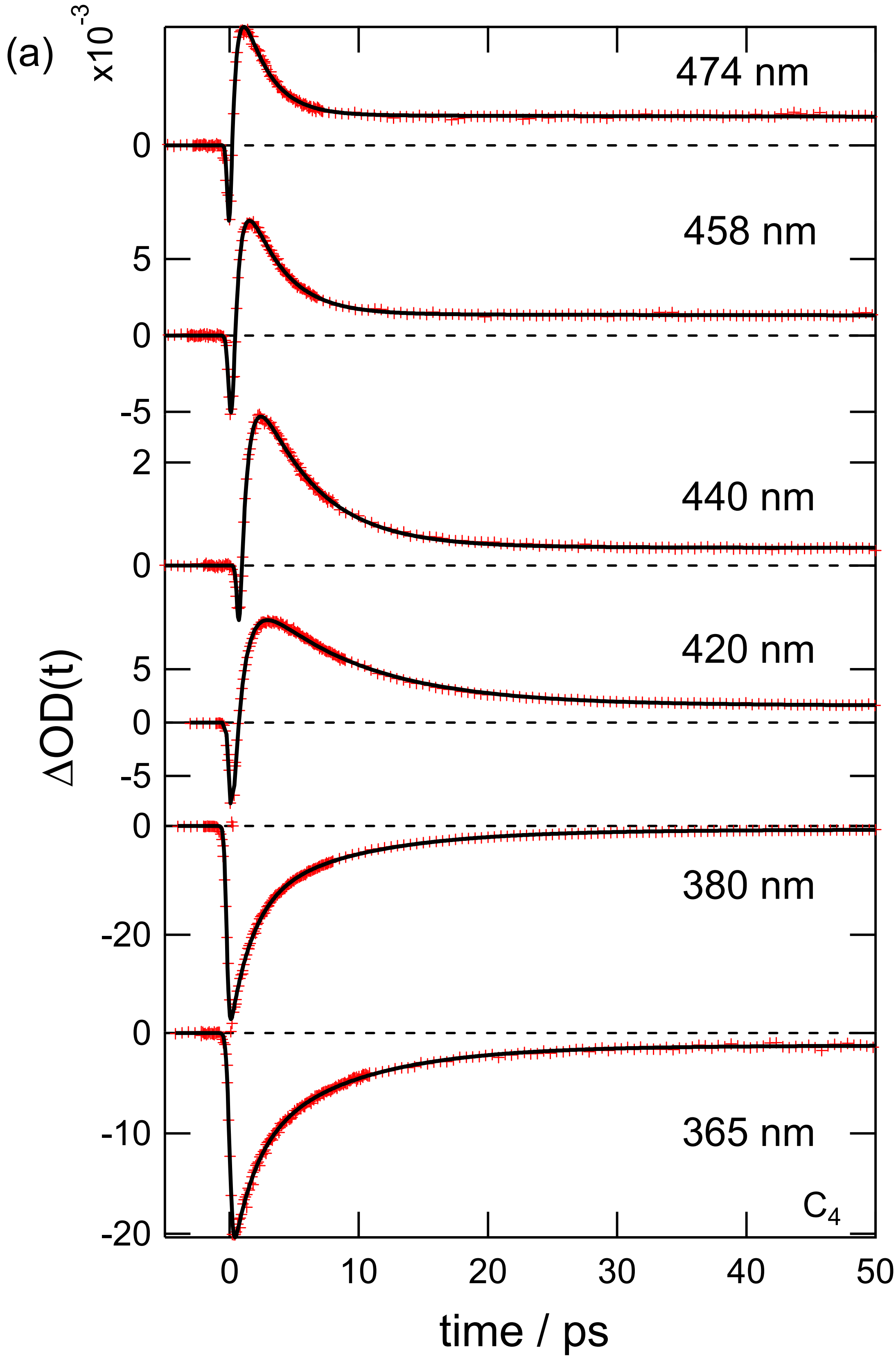
474 nm

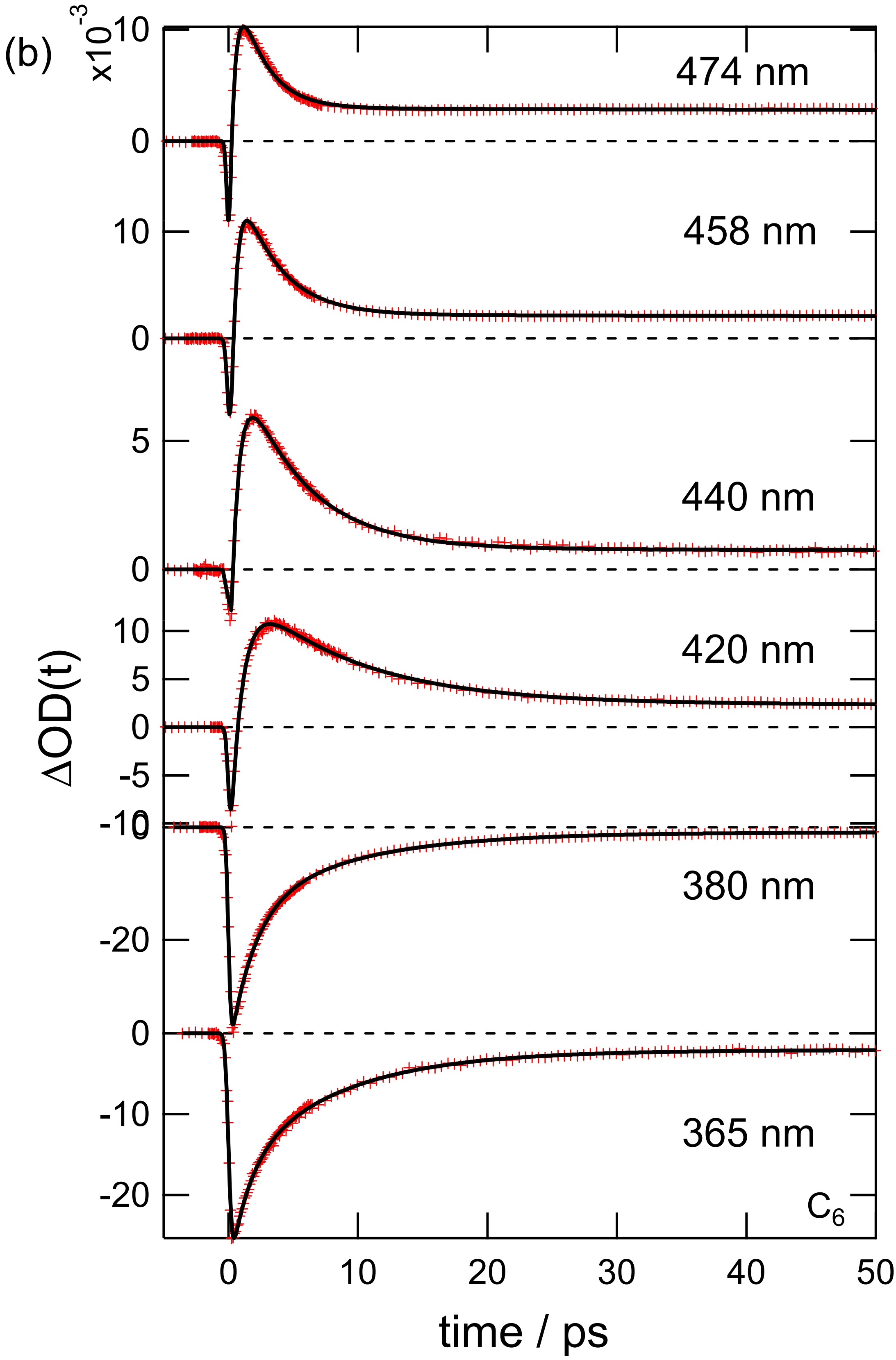
Cation	A_1	A_2	A_3	τ_1	τ_2
C_2mim^+	-1 ± 0.01	0.38 ± 0.02	0.015 ± 0.001	0.70 ± 0.01	3.9 ± 0.1
C_4mim^+	-1± 0.01	0.38 ± 0.02	0.022 ± 0.001	0.77 ± 0.01	4.0 ± 0.1
C_6mim^+	-1 ± 0.01	0.34 ± 0.03	0.025 ± 0.001	0.76 ± 0.01	4.7 ± 0.1
C_8mim^+	-1 ± 0.04	0.43 ± 0.03	0.029 ± 0.002	1.03 ± 0.05	4.4 ± 0.3
$C_{10}mim^+$	-1 ± 0.01	0.32 ± 0.03	0.033 ± 0.006	0.81 ± 0.01	4.2 ± 0.1
$C_{12}mim^+$	-1 ± 0.01	0.30 ± 0.05	0.045 ± 0.001	0.79 ± 0.01	4.7 ± 0.1

Table S3. Absorption maximum wavelength, the reaction free energy (ΔG) and the solvent reorganization energy (λ_S) estimated from the absorption spectrum using eq. (3), and the ratio of the calculated back-ET rate from eq. (4) for DMpNA in different ILs.

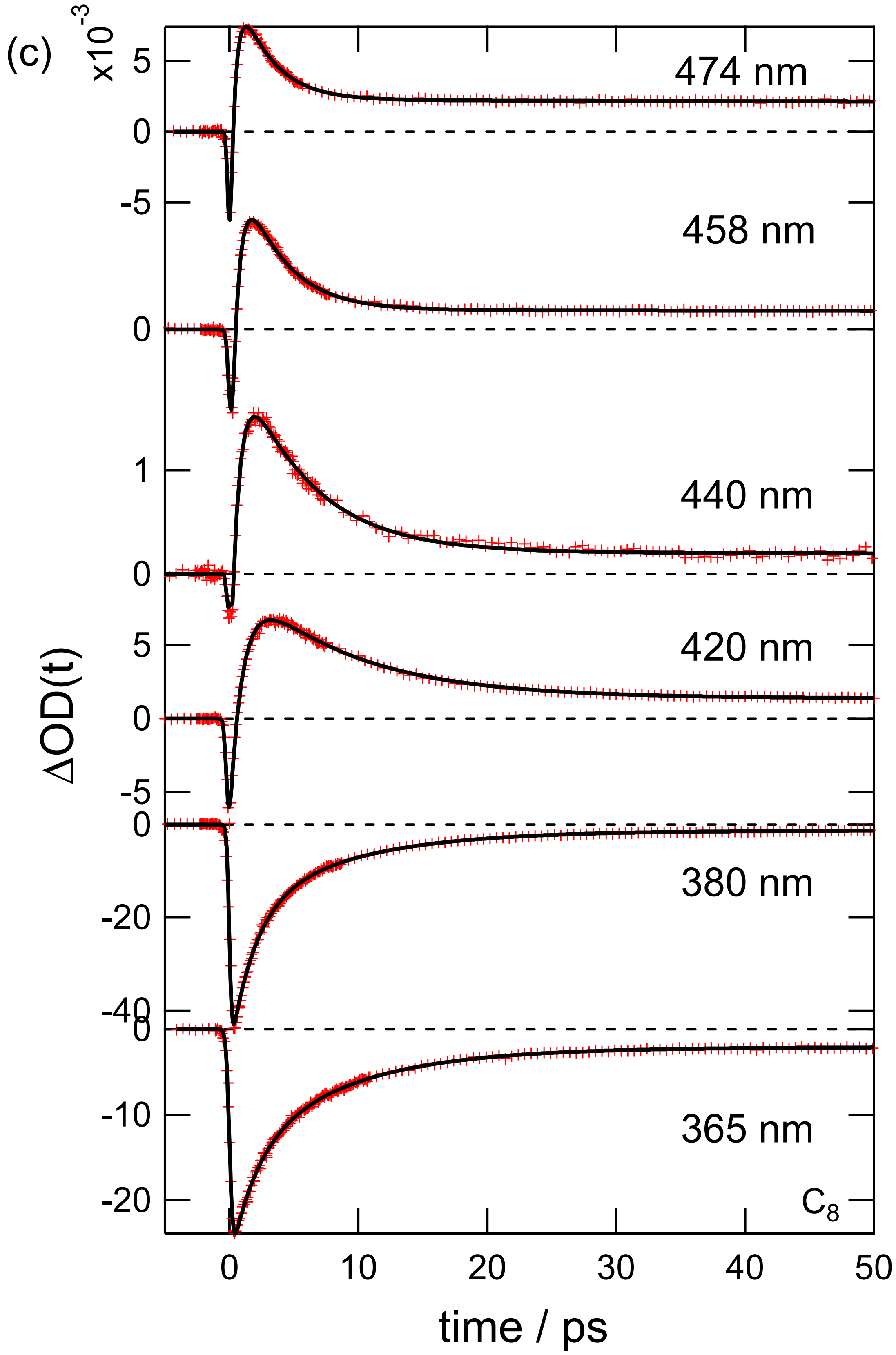
Cation	λ_{max}	ΔG / cm^{-1}	λ_S / cm^{-1}	$k_{et}([C_2mim][NTf_2])/k_{et}$
C_2mim^+	402.1	20990	3260	1.00
C_4mim^+	400.9	21120	3230	1.29
C_6mim^+	400.9	21240	3100	2.02
C_8mim^+	400.4	21320	3060	2.47
$C_{10}mim^+$	399.8	21400	3020	3.04
$C_{12}mim^+$	399.1	21430	3030	3.11

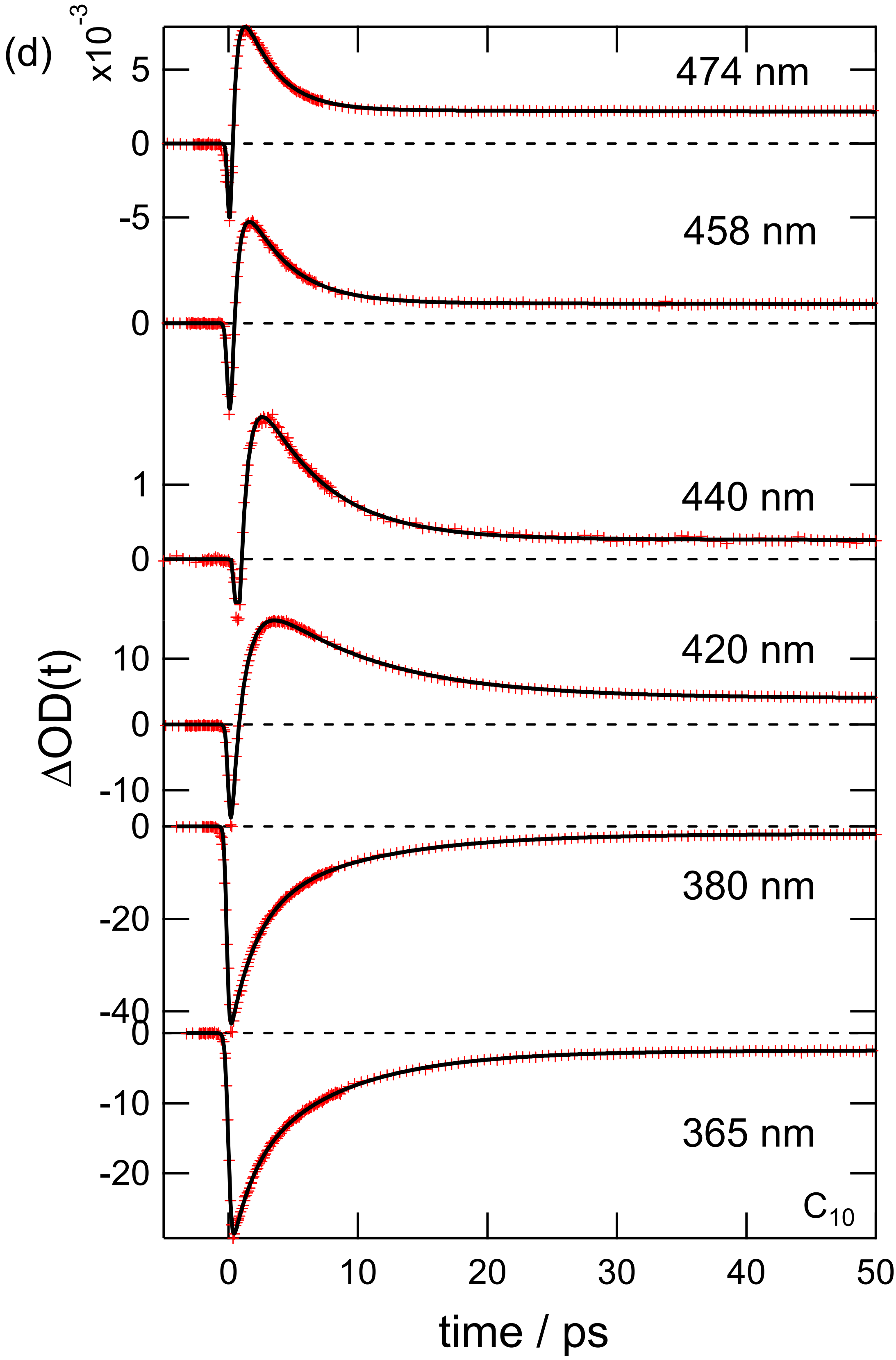
Figure S1 Time profiles of the transient absorption (ΔOD) of pNA at different probe wavelengths in (a)[C_4mim][NTf_2], (b) [C_6mim][NTf_2], (c) [C_8mim][NTf_2], (d) [C_{10}mim][NTf_2], and (e) [C_{12}mim][NTf_2]. The dashed lines indicate ΔOD = 0. The black lines are the results of fitting by a multi-exponential function.





(b)
x10^-3
474 nm
458 nm
440 nm
420 nm
380 nm
365 nm
C6
ΔOD(t)
time / ps


(c)
x10^-3
474 nm
458 nm
440 nm
420 nm
380 nm
365 nm
C8
ΔOD(t)
time / ps
5
0
-5
0
1
0
5
0
-5
0
-20
-40
0
-10
-20
0
10
20
30
40
50


(d)
x10^-3
474 nm
458 nm
440 nm
420 nm
380 nm
365 nm
C10
ΔOD(t)
time / ps
5
0
-5
0
1
0
10
0
-10
0
-20
-40
0
-10
-20
0
10
20
30
40
50

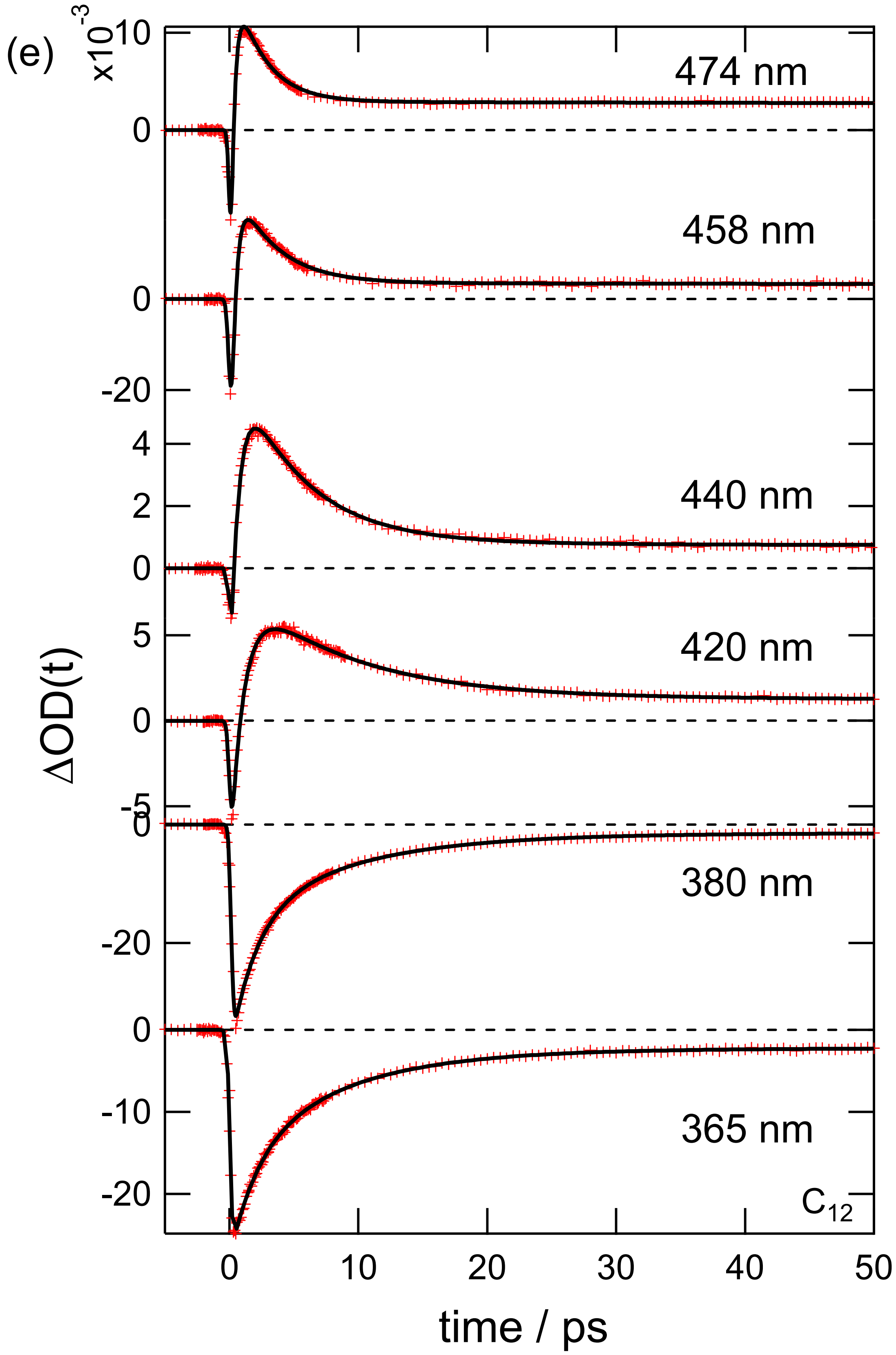
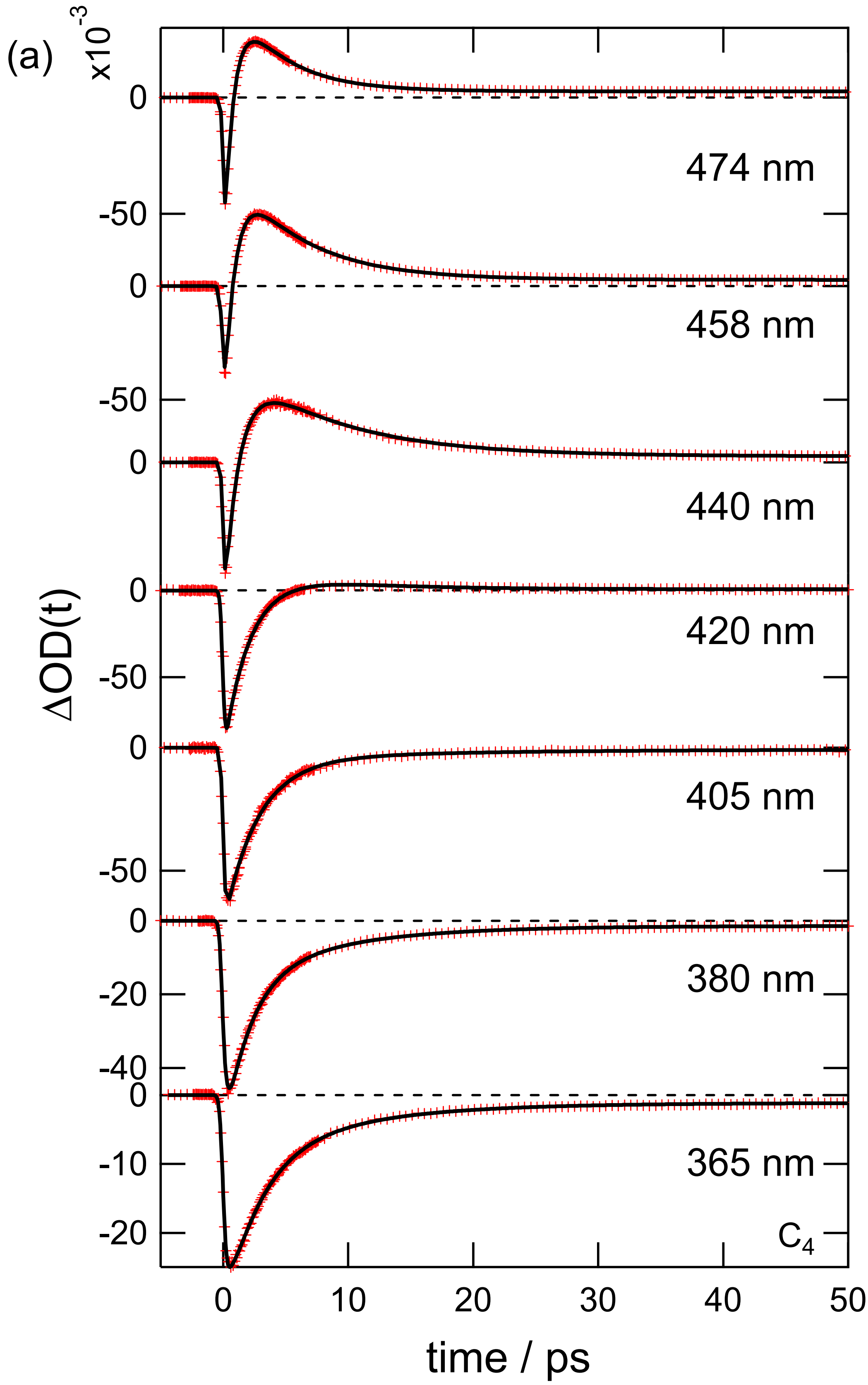
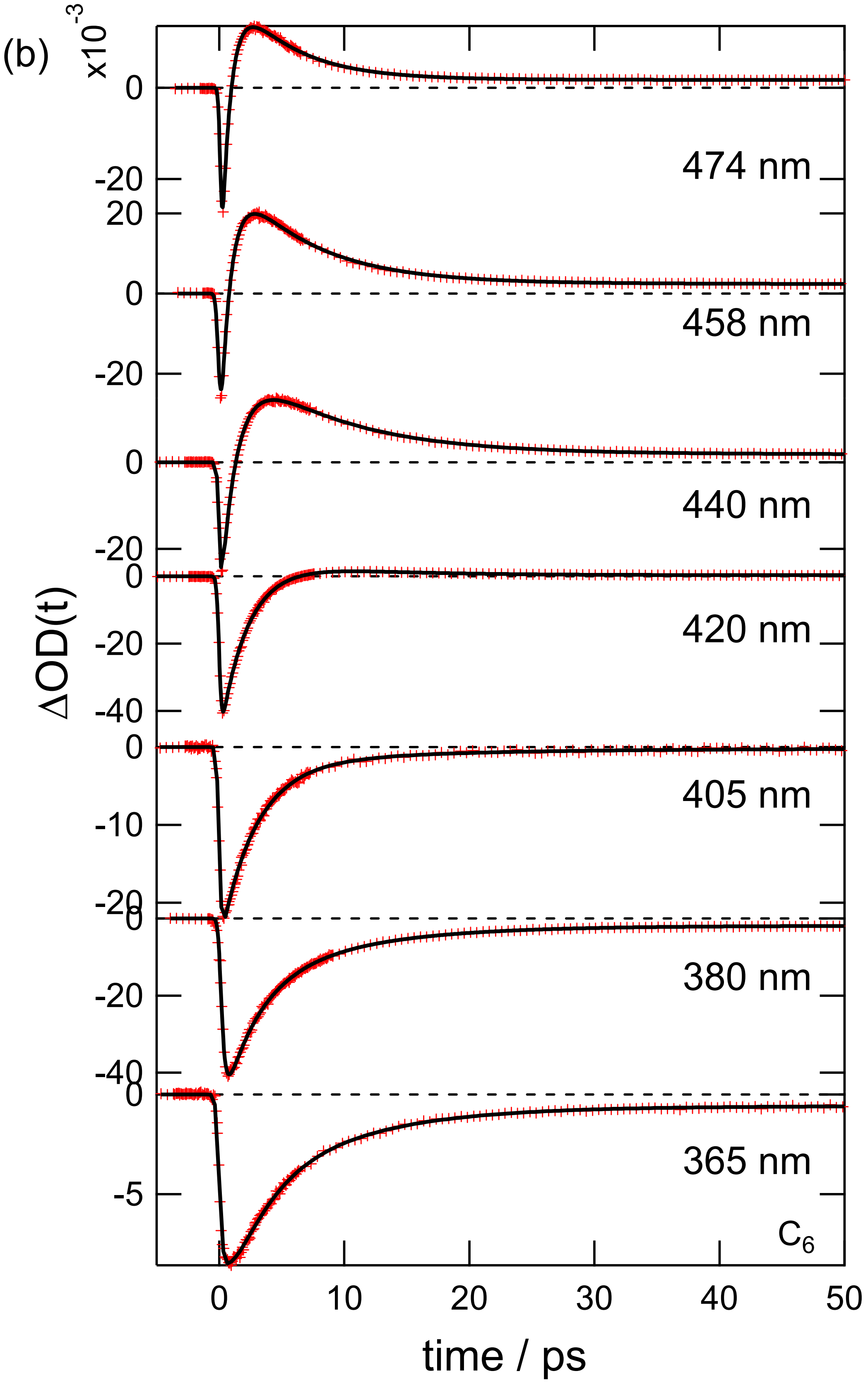
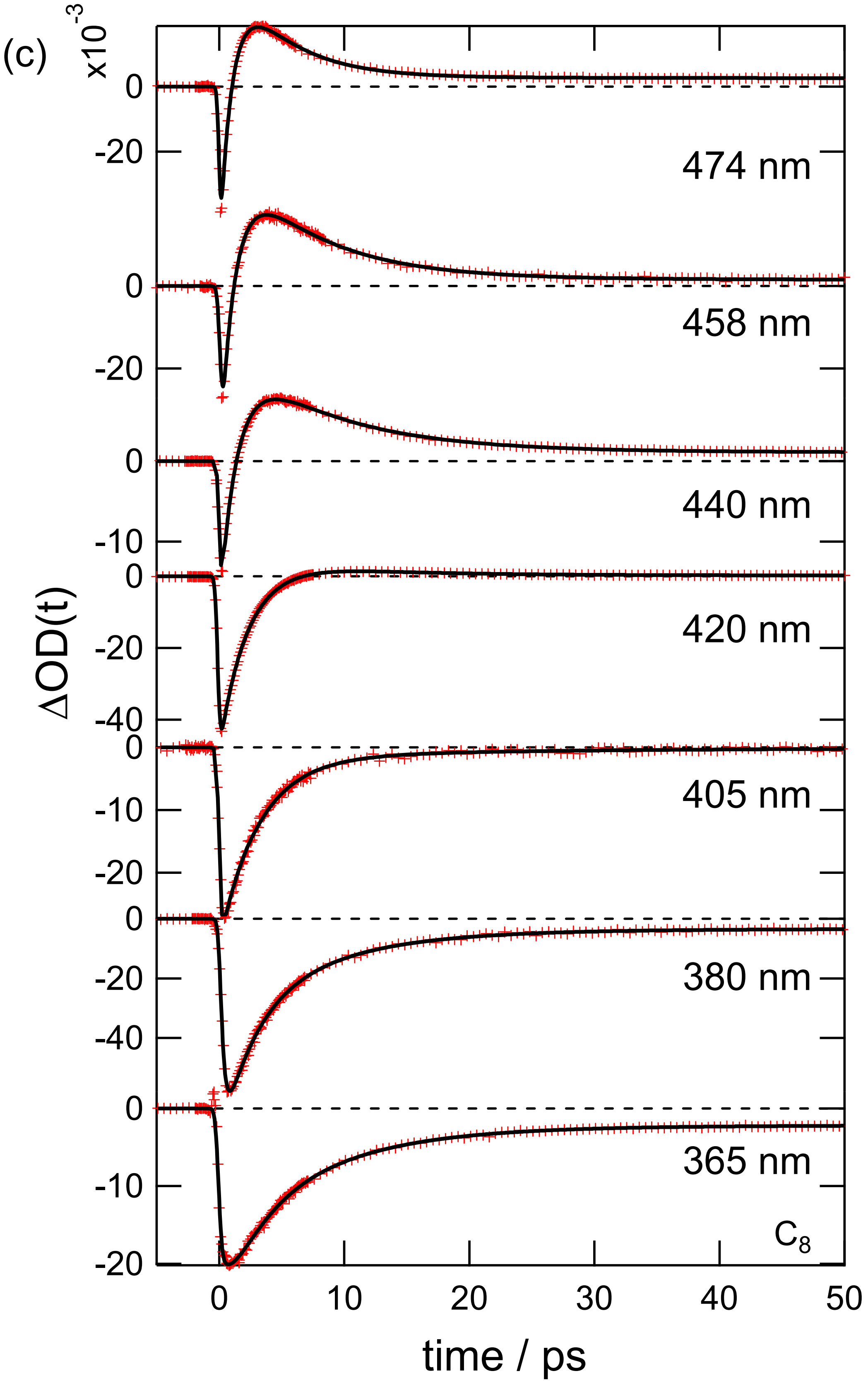

(e)
x10^-3
ΔOD(t)
474 nm
458 nm
440 nm
420 nm
380 nm
365 nm
C12
10
0
-20
4
2
5
-5
-10
20
30
40
50
time / ps

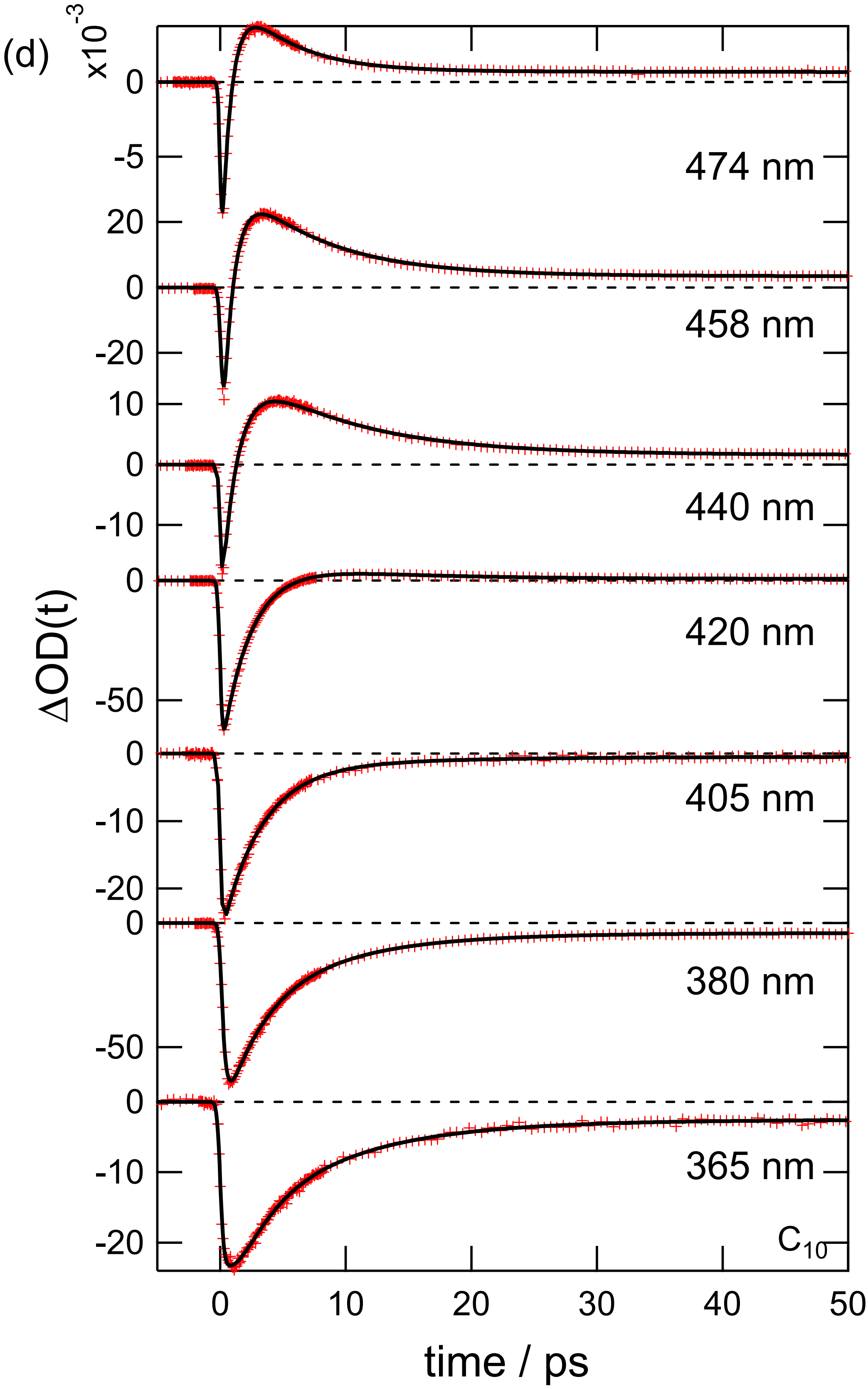
Figure S2. Time profiles of the transient absorption (ΔOD) of DMpNA at different probe wavelengths in (a)[C_4mim][NTf_2], (b) [C_6mim][NTf_2], (c) [C_8mim][NTf_2], (d) [C_{10}mim][NTf_2], and (e) [C_{12}mim][NTf_2]. The dashed lines indicate ΔOD = 0. The black lines are the results of fitting by a multi-exponential function.



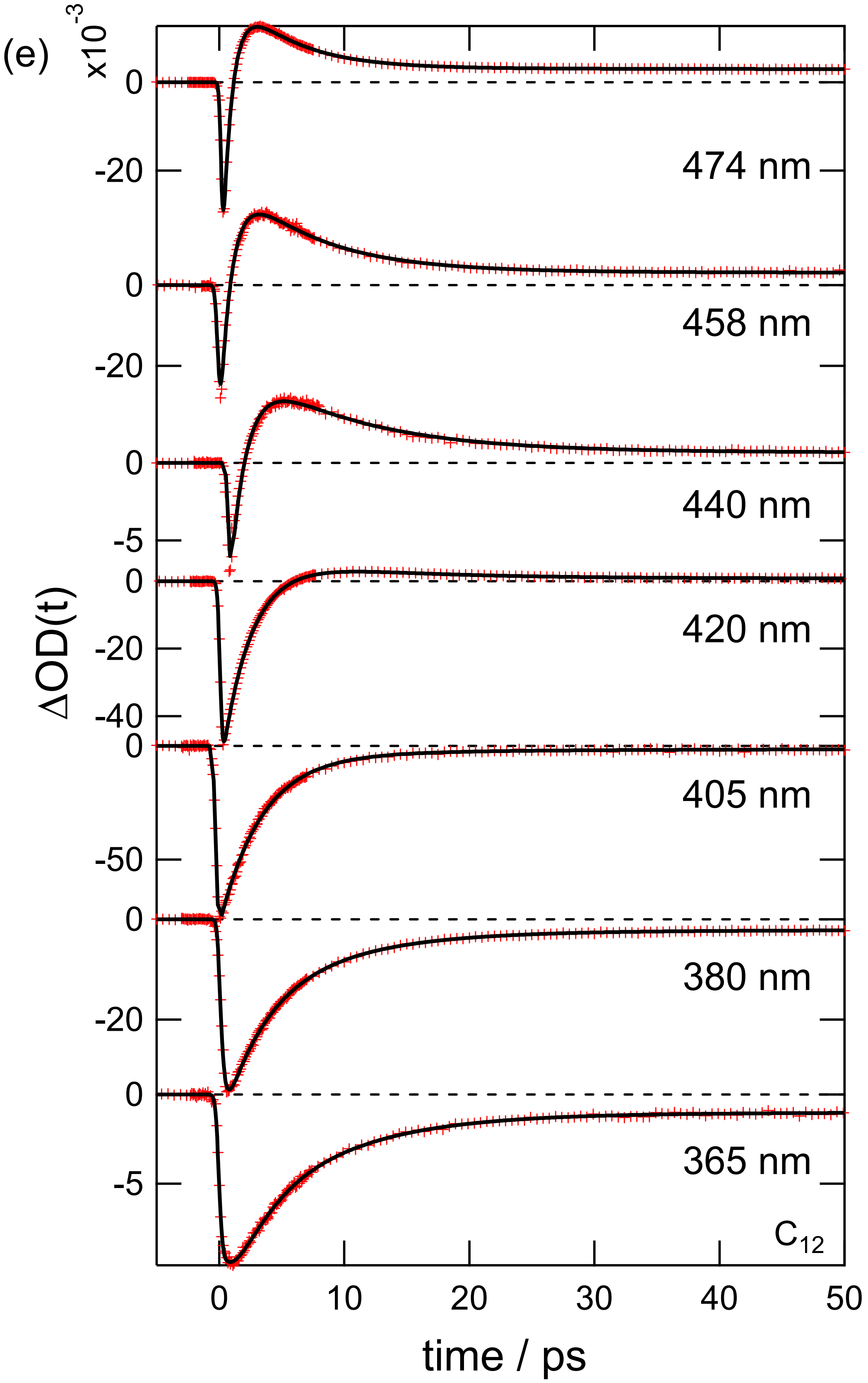

(b)
x10^-3
0
-20
474 nm
20
0
-20
458 nm
0
-20
440 nm
0
-20
-40
420 nm
0
-10
-20
405 nm
0
-20
-40
380 nm
0
-5
365 nm
C6
ΔOD(t)
0
10
20
30
40
50
time / ps



(c)
x10^-3
ΔOD(t)
474 nm
458 nm
440 nm
420 nm
405 nm
380 nm
365 nm
C8
time / ps



(d)
x10^-3
ΔOD(t)
474 nm
458 nm
440 nm
420 nm
405 nm
380 nm
365 nm
C10
time / ps



(e)
x10^-3
0
-20
474 nm
0
-20
458 nm
0
-5
440 nm
0
-20
-40
420 nm
0
-50
405 nm
0
-20
380 nm
0
-5
365 nm
C12
ΔOD(t)
0
10
20
30
40
50
time / ps

Figure S3. Example of the spectral simulation by eq.(3) for DMpNA in $[C_{12}mim][NTf_2]$. The black solid curve is the experimental absorption spectrum and the red curve is the calculated one.