Figures

Figure S1. The differential spectra accompanying the formation of a Cu(III) species from Cu(II)-TESHHK- complexes (0.5 mM) upon the addition of 1 mM H_2O_2 at pH 7.4 (50 mM phosphate buffer) and 37 °C. The first spectrum was recorded at 0.5 min after the H_2O_2 addition, and the following ones in 2 min. intervals.

Figure S2. The differential spectra accompanying the formation of a Cu(III) species from Cu(II)-TASHHK- complexes (0.5 mM) upon the addition of 1 mM H_2O_2 at pH 7.4 (50 mM phosphate buffer) and 37 °C. The first spectrum was recorded at 0.5 min after the H_2O_2 addition, and the following ones in 2 min. intervals.

Figure S3. The differential spectra accompanying the formation of a Cu(III) species from Cu(II)-TESAHK- complexes (0.5 mM) upon the addition of 1 mM H_2O_2 at pH 7.4 (50 mM phosphate buffer) and 37 °C. The first spectrum was recorded at 0.5 min after the H_2O_2 addition, and the following ones in 2 min. intervals.

Figure S4. The differential spectra accompanying the formation of a Cu(III) species from Cu(II)-TESHAK- complexes (0.5 mM) upon the addition of 1 mM H_2O_2 at pH 7.4 (50 mM phosphate buffer) and 37 °C. The first spectrum was recorded at 0.5 min after the H_2O_2 addition, and the following ones in 2 min. intervals.

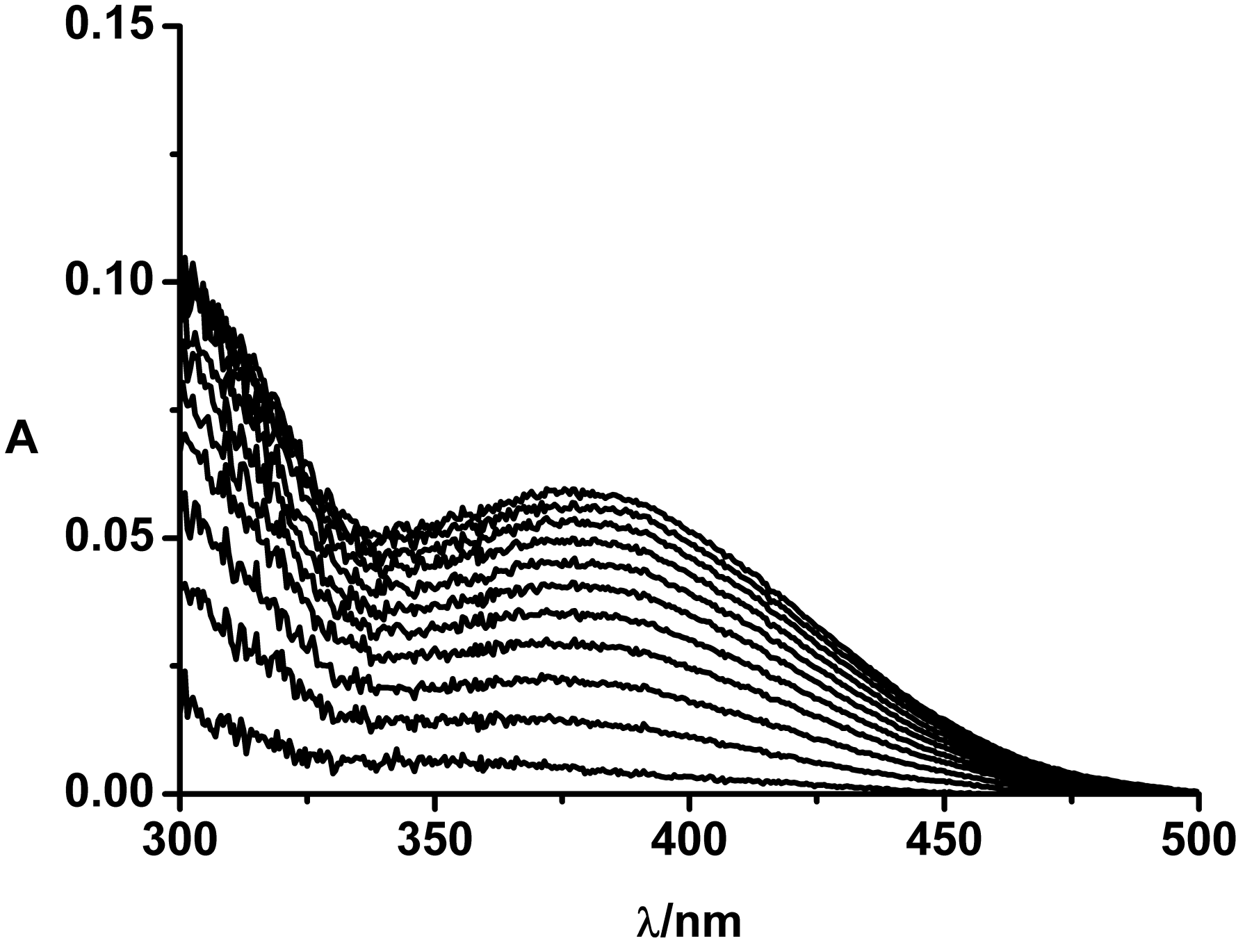
Figure S5. Species distribution for Cu(II)-TESHHK- complexes, calculated for reagent concentrations used in kinetics measurements, using the binding constants published previously.[3,4] The pseudo-first-order rate constants for $HO^{\bullet}$ k (!) are overlaid. The reaction mixture was incubated at 37 °C and contained: Cu(II)-TESHHK- (0.5 mM), H_2O_2 (1 mM), NDMA (2.5×10^{-5} M), phosphate buffer (50 mM, pH 7.4).

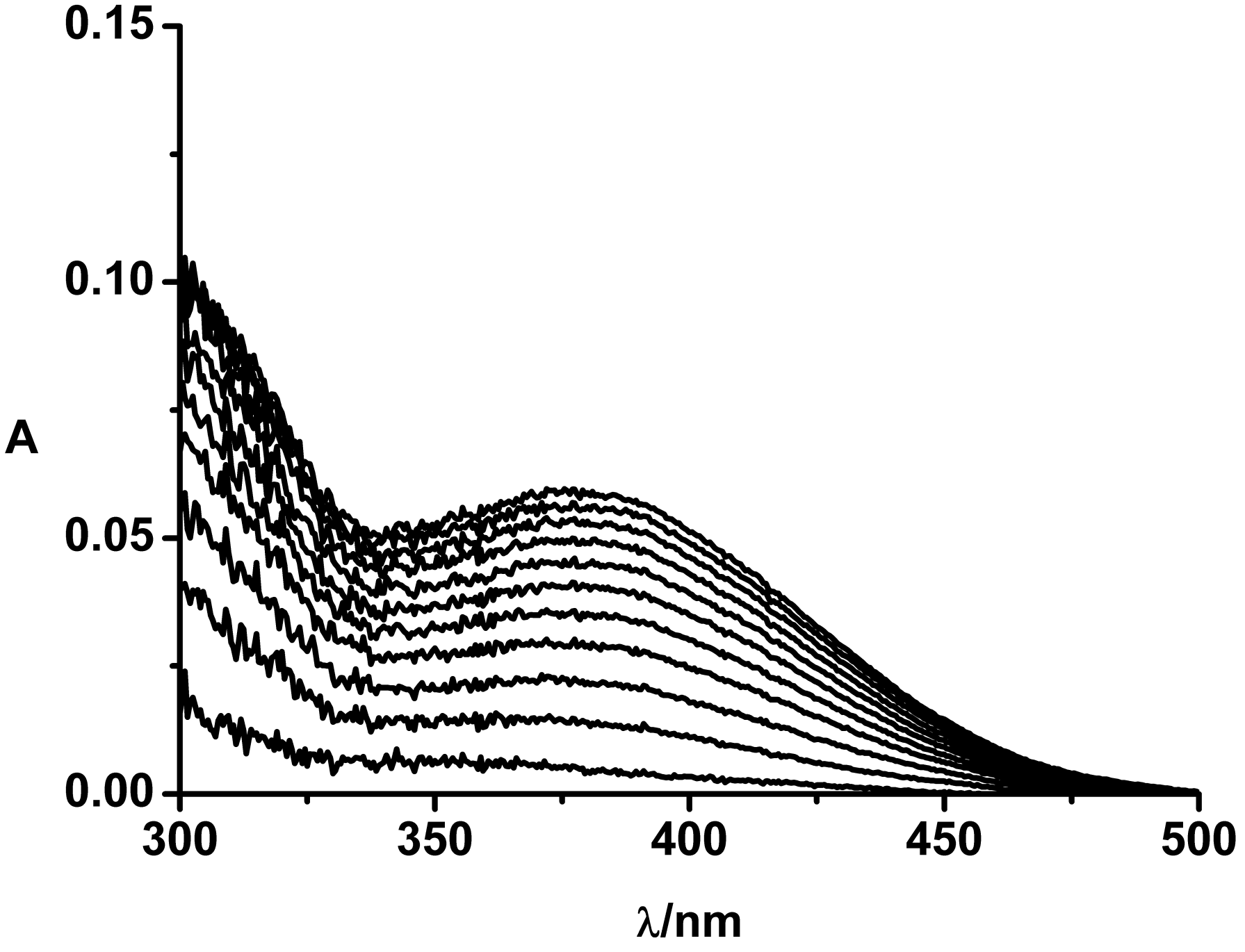
Figure S6. Species distribution for Cu(II)-TASHHK- complexes, calculated for reagent

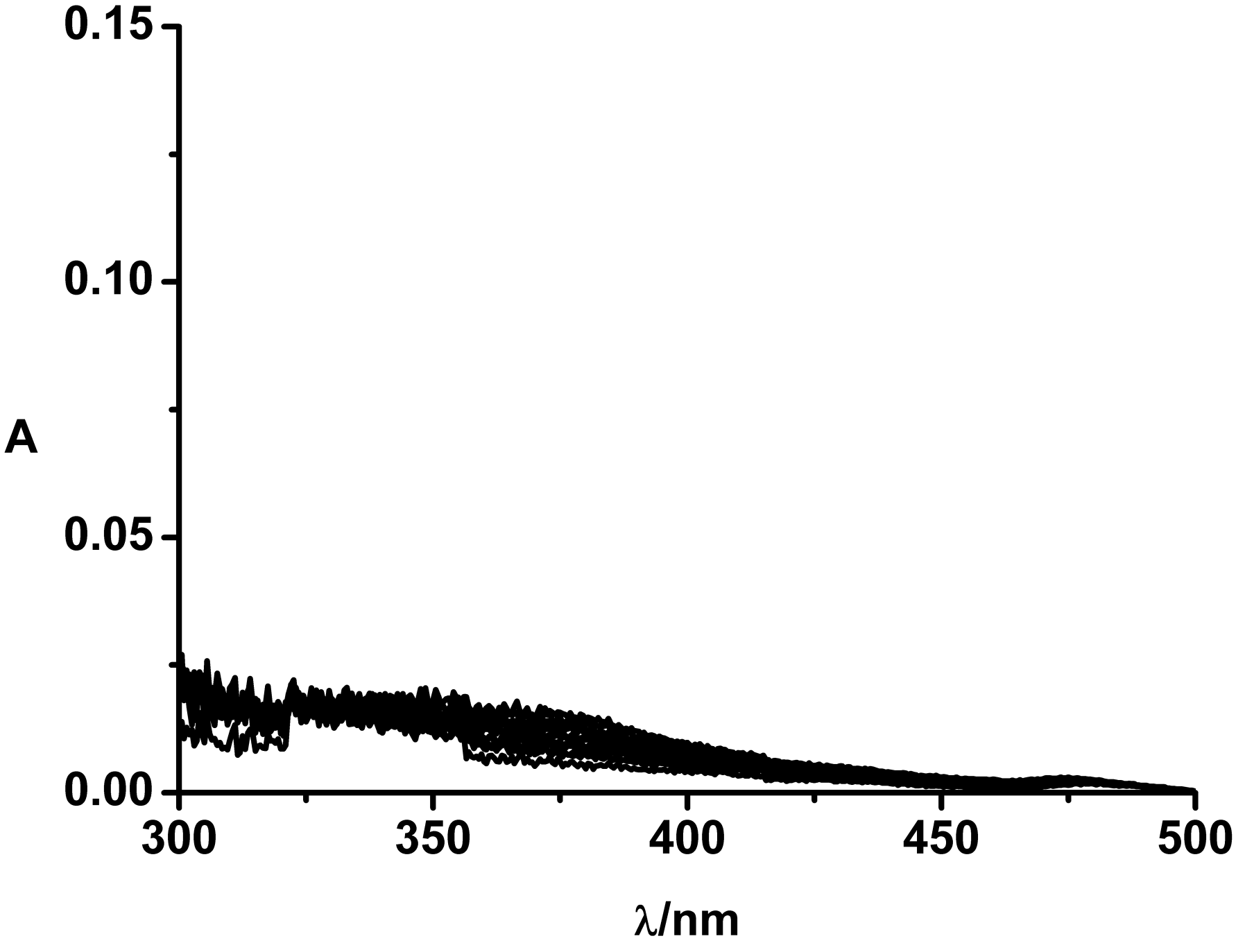
concentrations used in kinetics measurements, using the binding constants published previously.[3,4] The pseudo-first-order rate constants for $HO^{\bullet}$ k (!) are overlaid. The reaction mixture was incubated at 37 °C and contained: Cu(II)-TASHHK- (0.5 mM), H_2O_2 (1 mM), NDMA (2.5×10^{-5} M), phosphate buffer (50 mM, pH 7.4).

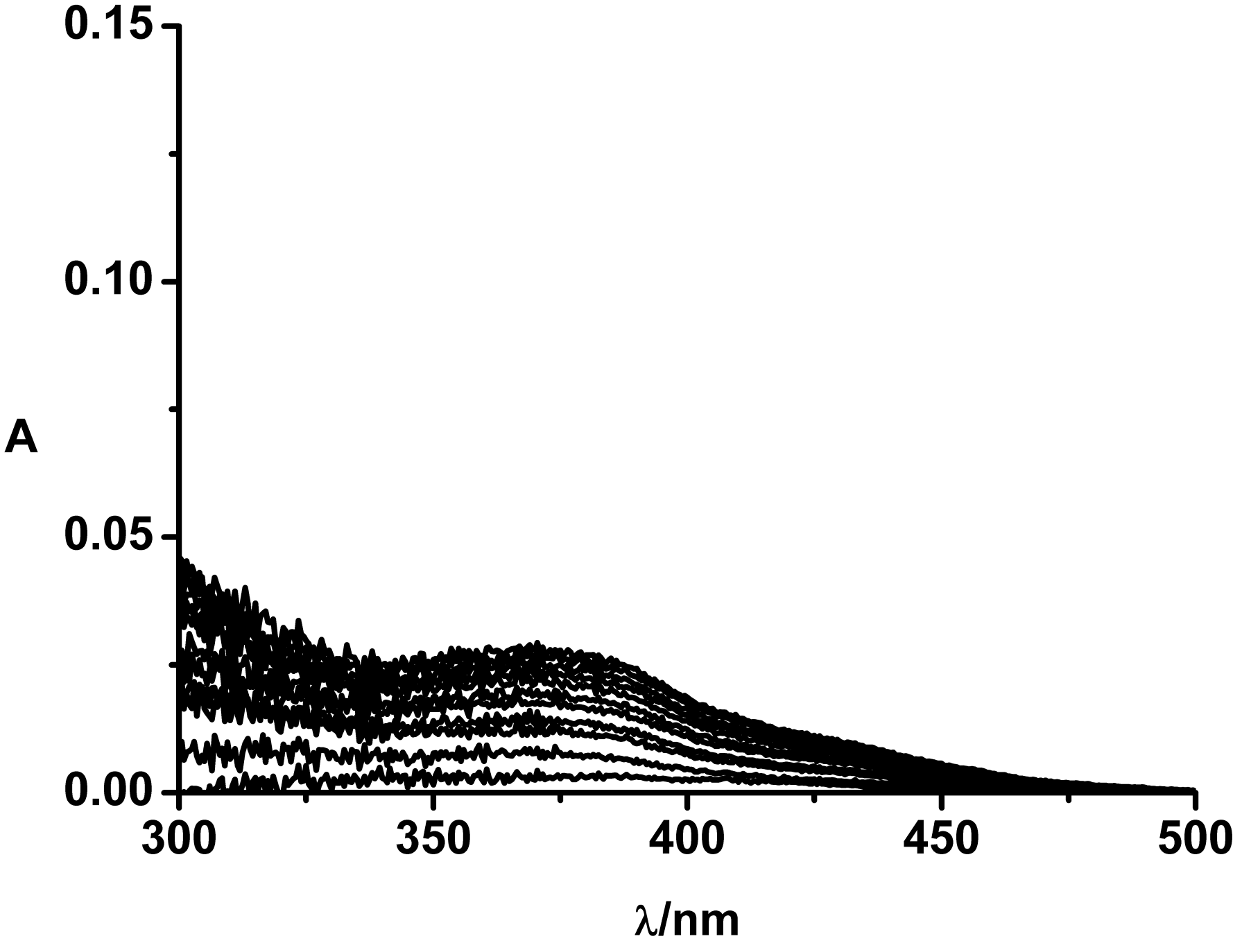
Figure S7. Species distribution for Cu(II)-TESAHK- complexes, calculated for reagent concentrations used in kinetics measurements, using the binding constants published previously.[3,4] The pseudo-first-order rate constants for $HO^{\bullet}$ k (!) are overlaid. The reaction mixture was incubated at 37 °C and contained: Cu(II)-TESAHK- (0.5 mM), H_2O_2 (1 mM), NDMA (2.5×10^{-5} M), phosphate buffer (50 mM, pH 7.4).

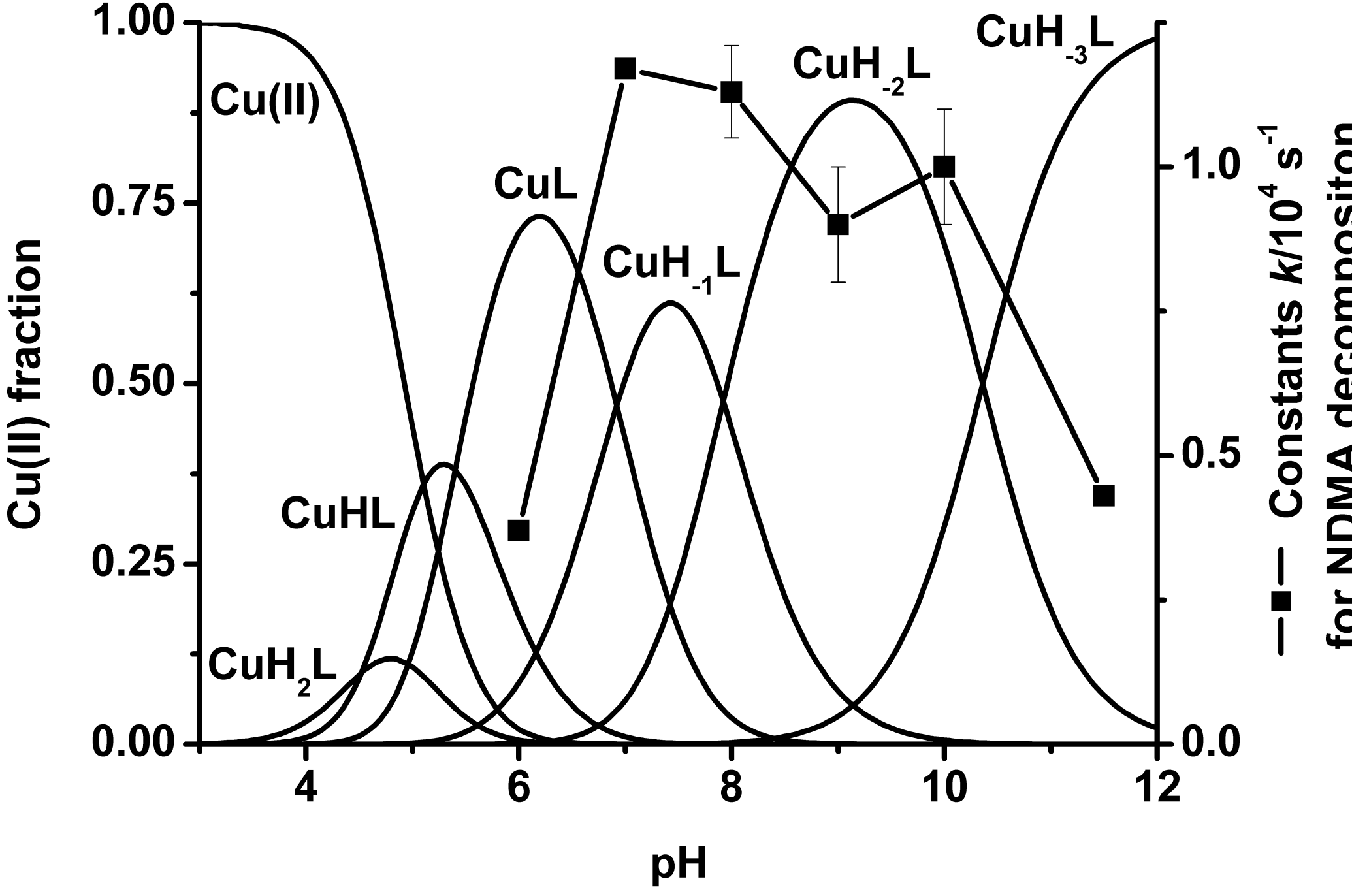
Figure S6. Species distribution for Cu(II)-TESHAK- complexes, calculated for reagent concentrations used in kinetics measurements, using the binding constants published previously.[3,4] The pseudo-first-order rate constants for $HO^{\bullet}$ k (!) are overlaid. The reaction mixture was incubated at 37 °C and contained: Cu(II)-TESHAK- (0.5 mM), H_2O_2 (1 mM), NDMA (2.5×10^{-5} M), phosphate buffer (50 mM, pH 7.4).

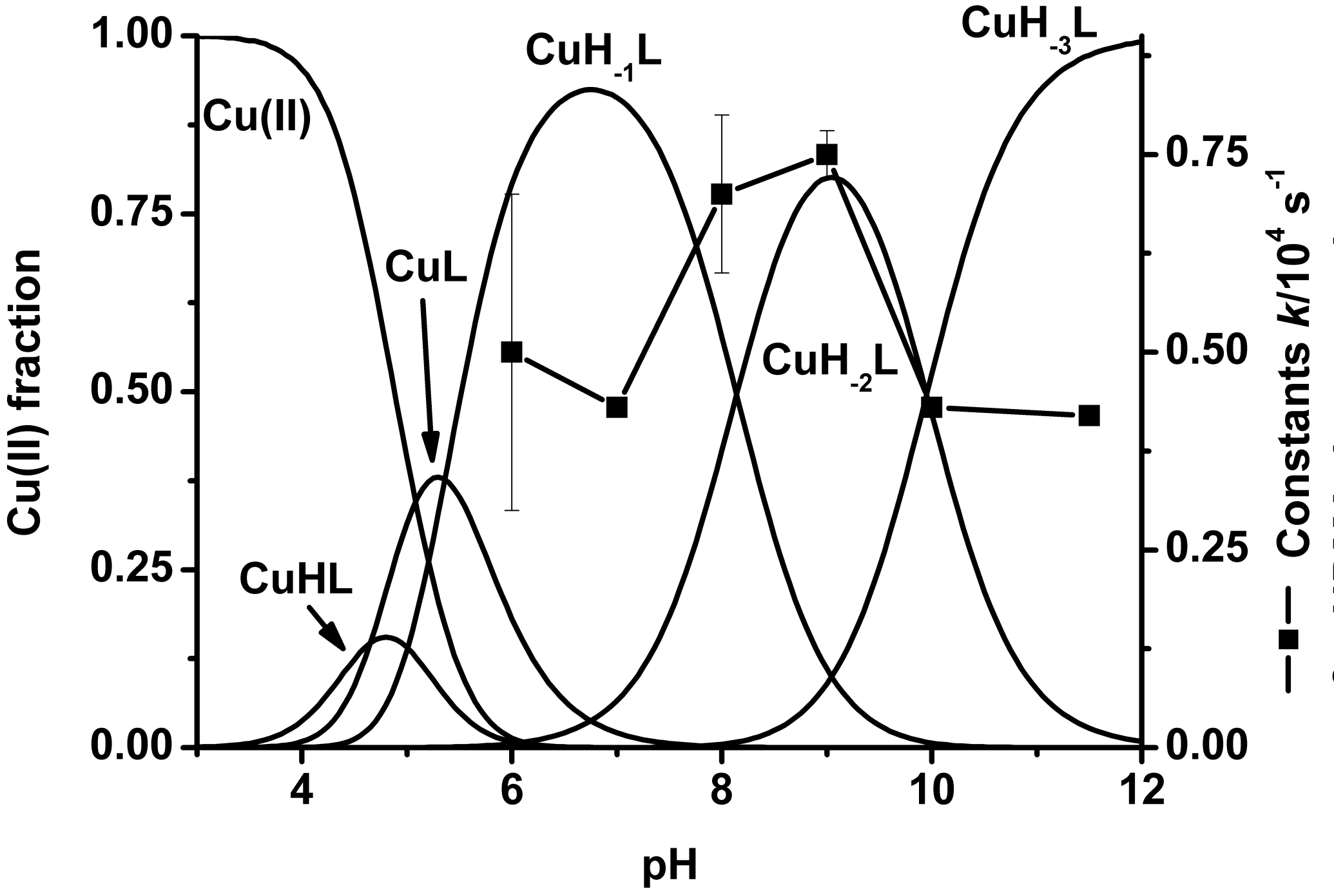

0.15
0.10
0.05
0.00
A
300
350
400
450
500
λ/nm

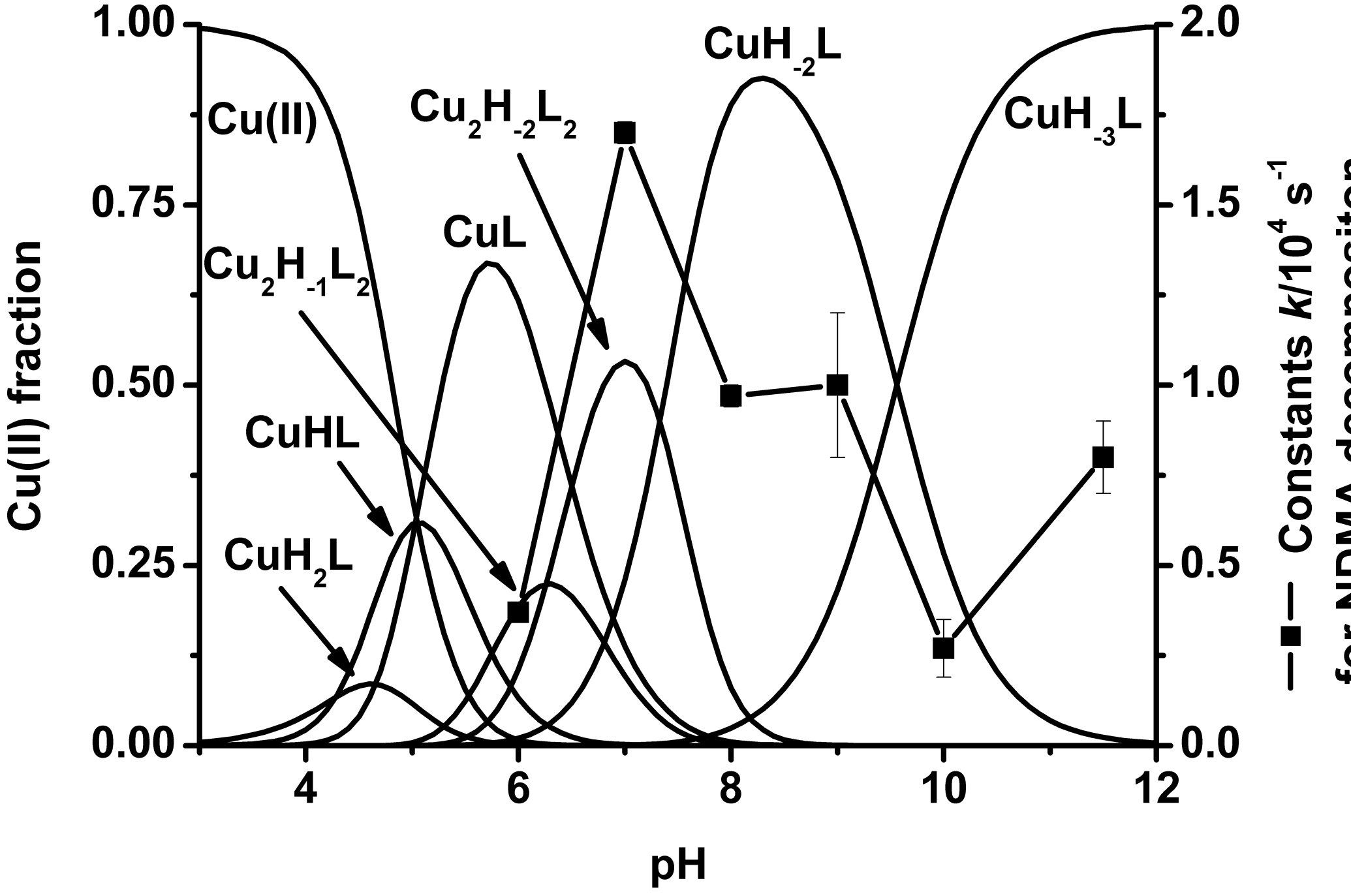

0.15
0.10
0.05
0.00
A
300
350
400
450
500
λ/nm

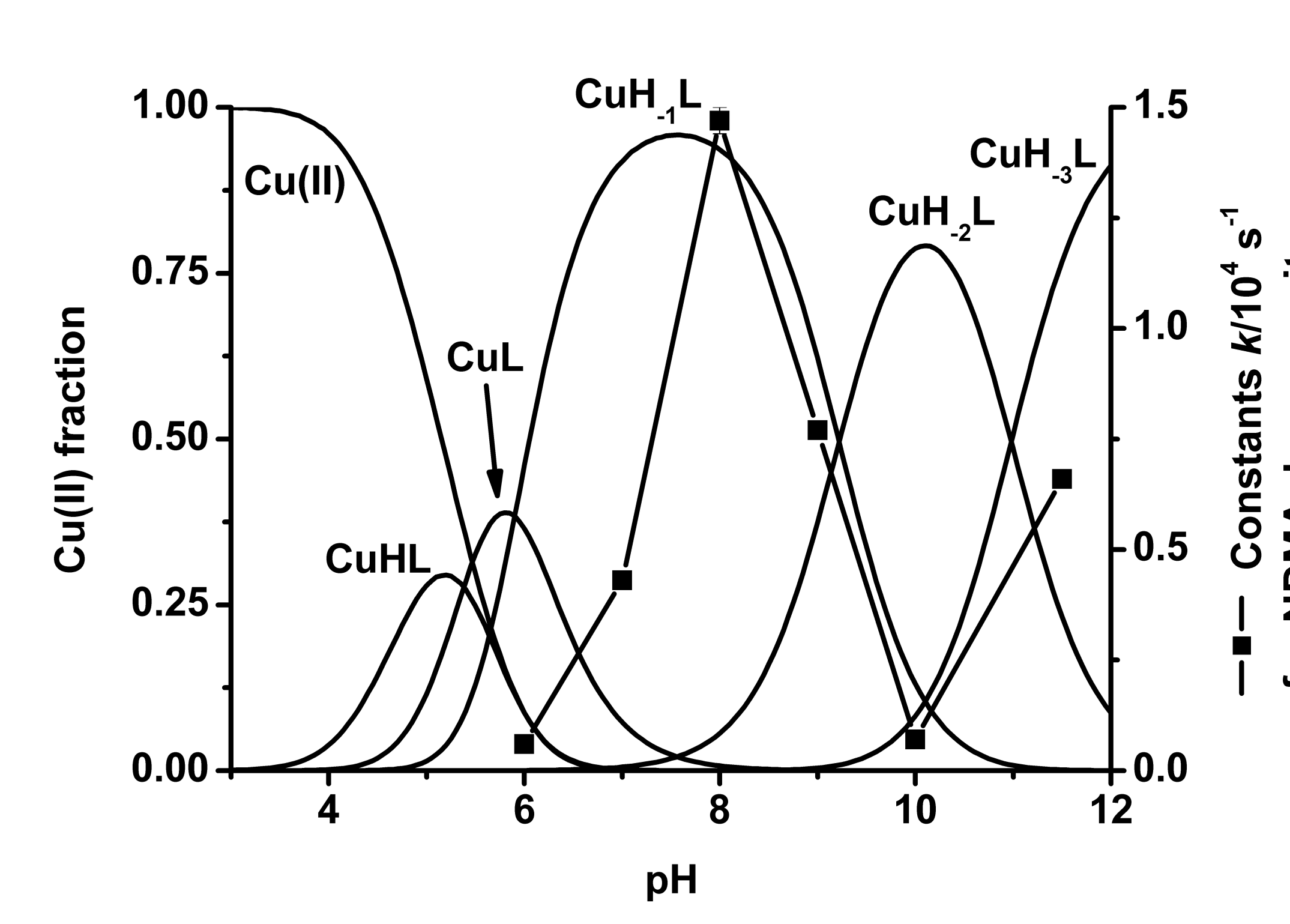

0.15
0.10
0.05
0.00
A
300
350
400
450
500
λ/nm


0.15
0.10
0.05
0.00
A
300
350
400
450
500
λ/nm


1.00
0.75
0.50
0.25
0.00
Cu(II) fraction
Cu(II)
CuHL
CuH2L
CuL
CuH-1L
CuH-2L
CuH-3L
4
6
8
10
12
pH
1.0
0.5
0.0
—■— Constants k/10^4 s^-1
for NDMA decomposit


1.00
0.75
0.50
0.25
0.00
Cu(II) fraction
Cu(II)
CuHL
CuL
CuH-1L
CuH-2L
CuH-3L
4
6
8
10
12
pH
0.75
0.50
0.25
0.00
Constants k/10^4 s^-1


1.00
0.75
0.50
0.25
0.00
Cu(II) fraction
Cu(II)
Cu2H-1L2
CuHL
CuH2L
Cu2H-2L2
CuL
CuH-2L
CuH-3L
4
6
8
10
12
pH
2.0
1.5
1.0
0.5
0.0
Constants k/10^4 s^-1


Cu(II)
CuHL
CuL
CuH-1L
CuH-2L
CuH-3L
Cu(II) fraction
Constants k/10^4 s^-1
pH
1.00
0.75
0.50
0.25
0.00
1.5
1.0
0.5
0.0
4
6
8
10
12

Tables

Table S1. Linear correlation between the positions of reduction peaks and the pH of the samples.

peptide	intercept	slope	R parameter
-TESHHK-	-0.98(4)	-0.023(5)	0.94379
	-0.18(9)	-0.05(1)	0.89137
-TASHHK-	-0.98(4)	-0.025(5)	0.94191
	0.02(9)	-0.06(1)	0.90021
-TEAHHK-	-1.00(2)	-0.018(2)	0.97984
	-0.36(4)	-0.022(5)	0.92079
-TESAHK-	-0.9(2)	-0.03(2)	0.62058
	-0.2(1)	-0.05(1)	0.88746
-TESHAK-	-0.50(4)	-0.008(4)	0.82034
	0.22(8)	-0.103(9)	0.99248