SUPPORTING INFORMATION

FIGURE 1: Regions of TOCSY spectra of PpcA (A) and PpcAF15Y (B) in the reduced form at 274K and pH 6.0. The aromatic ring protons of F41 and F15 are indicated. The connectivities between the thioether methine and thioether methyl of each heme groups are also indicated: **1**, 3^1H^{III} - $3^2CH_3^{III}$; **2**, 8^1H^{III} - $8^2CH_3^{III}$; **3**, 3^1H^{I} - $3^2CH_3^{I}$; **4**, 8^1H^{I} - $8^2CH_3^{I}$; **5**, 8^1H^{IV} - $8^2CH_3^{IV}$; **6**, 3^1H^{IV} - $3^2CH_3^{IV}$.

FIGURE 2: Portion of EXSY spectra of PpcA obtained at two different oxidation levels at pH 8.2 and 274 K. Cross peaks connecting the signals of the heme metyls $12^1CH_3^{I}$ (green), $7^1CH_3^{III}$ (red) and $12^1CH_3^{IV}$ (blue) in different oxidation stages are indicated by dashed lines. The Roman and Arabic numbers indicate the heme groups and the oxidation stages, respectively.

FIGURE 3: Redox titration followed by visible spectroscopy for PpcA at pH 6.9 and 298K. The main graphic shows the plot of the molar fraction of the total reduced protein fitted to the model for calculation of the macroscopic reduction potentials described in Materials and Methods section. The inset shows the α-band region of the visible spectra used for the potentiometric titration.

Fig. 1

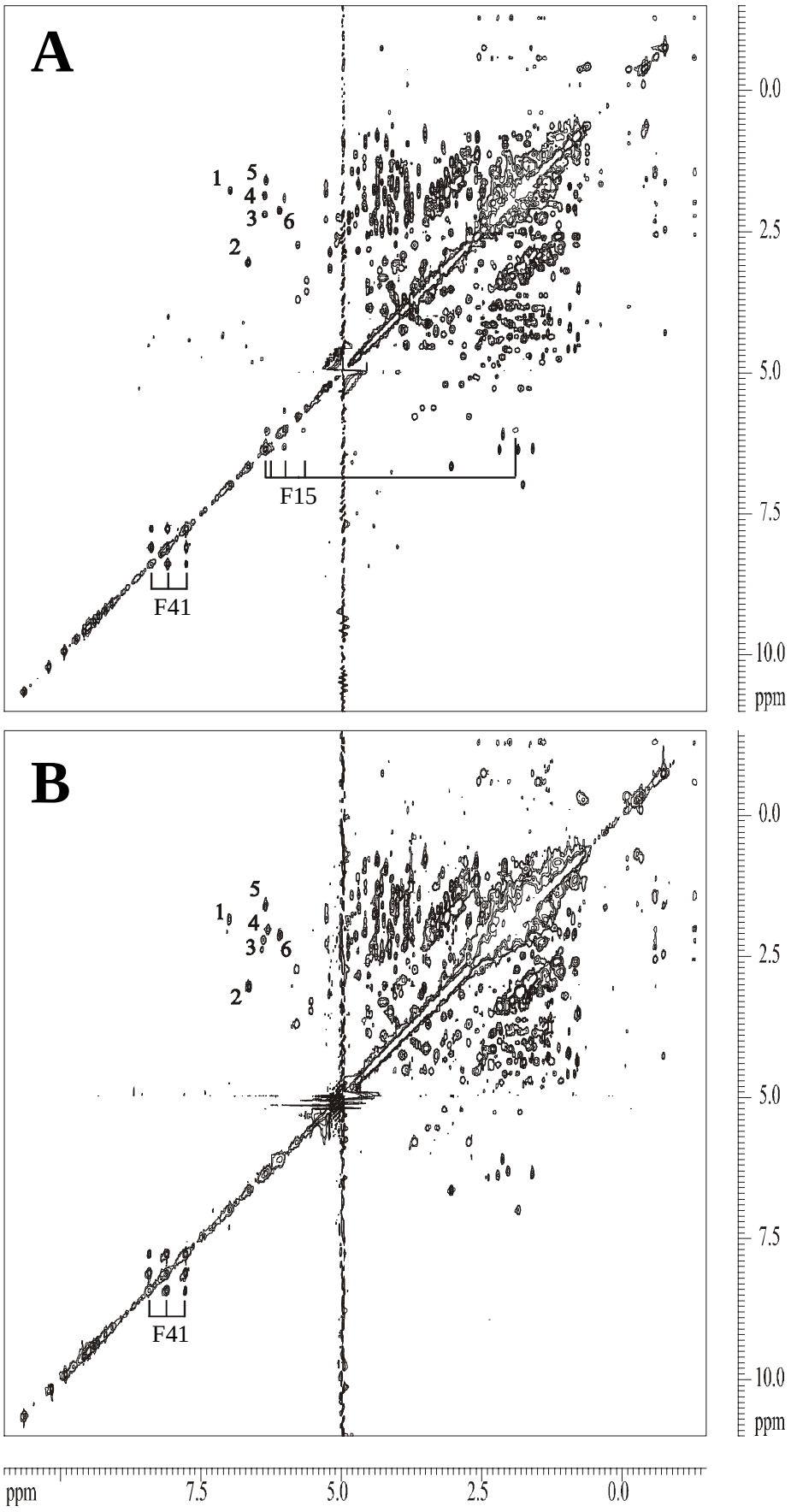

A
1
5
4
3
6
2
F15
F41
0.0
2.5
5.0
7.5
10.0
ppm
B
1
5
4
3
6
2
F41
0.0
2.5
5.0
7.5
10.0
ppm
ppm
7.5
5.0
2.5
0.0

Fig. 2

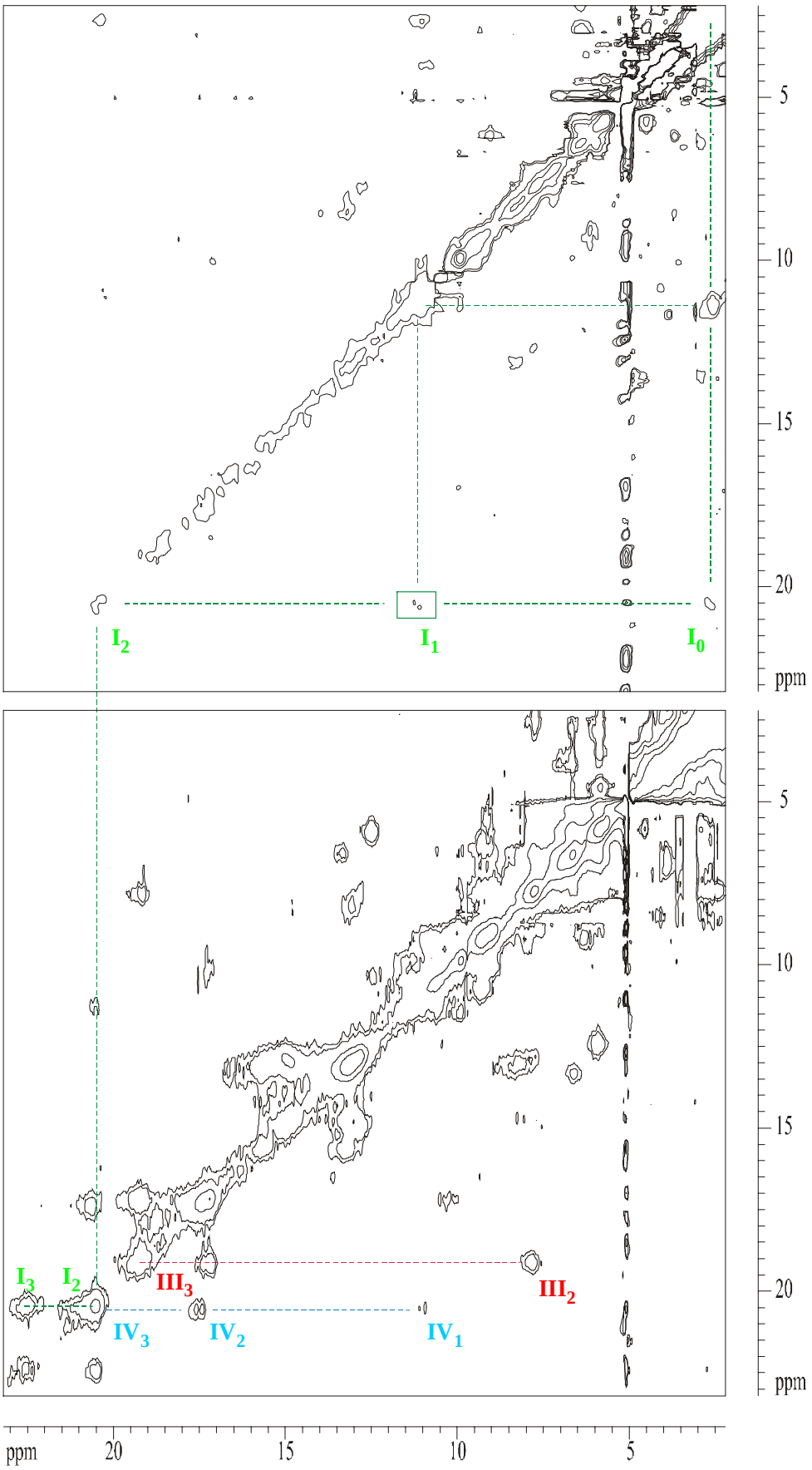
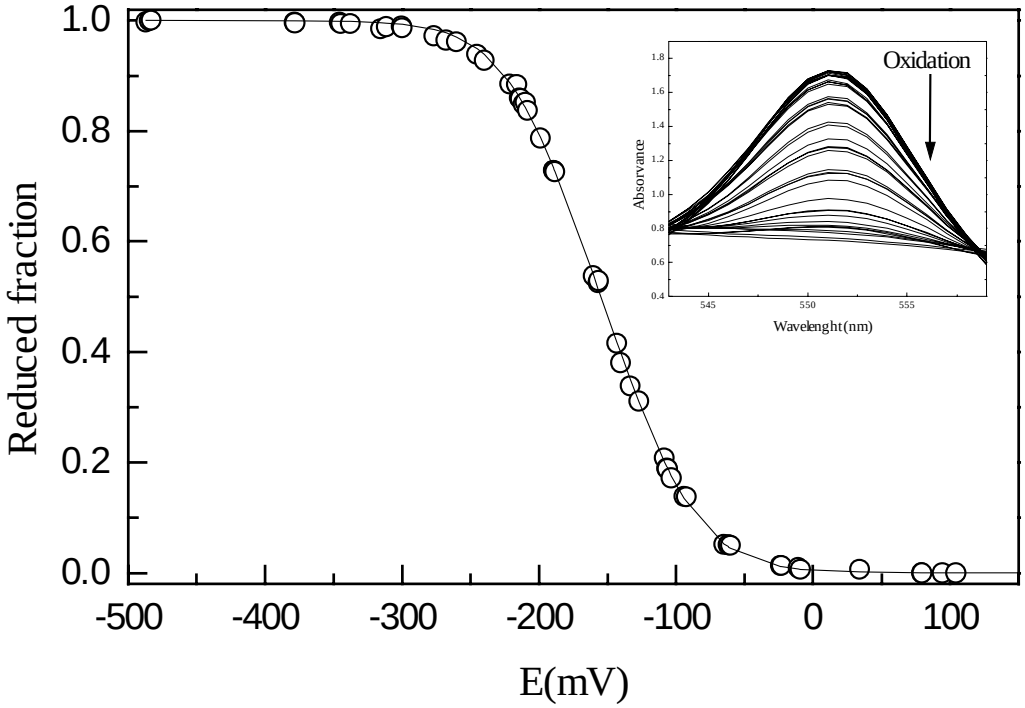


Fig. 3


Reduced fraction
E(mV)
1.0
0.8
0.6
0.4
0.2
0.0
-500
-400
-300
-200
-100
0
100
Oxidation
Absorvance
Wavelenght (nm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
545
550
555