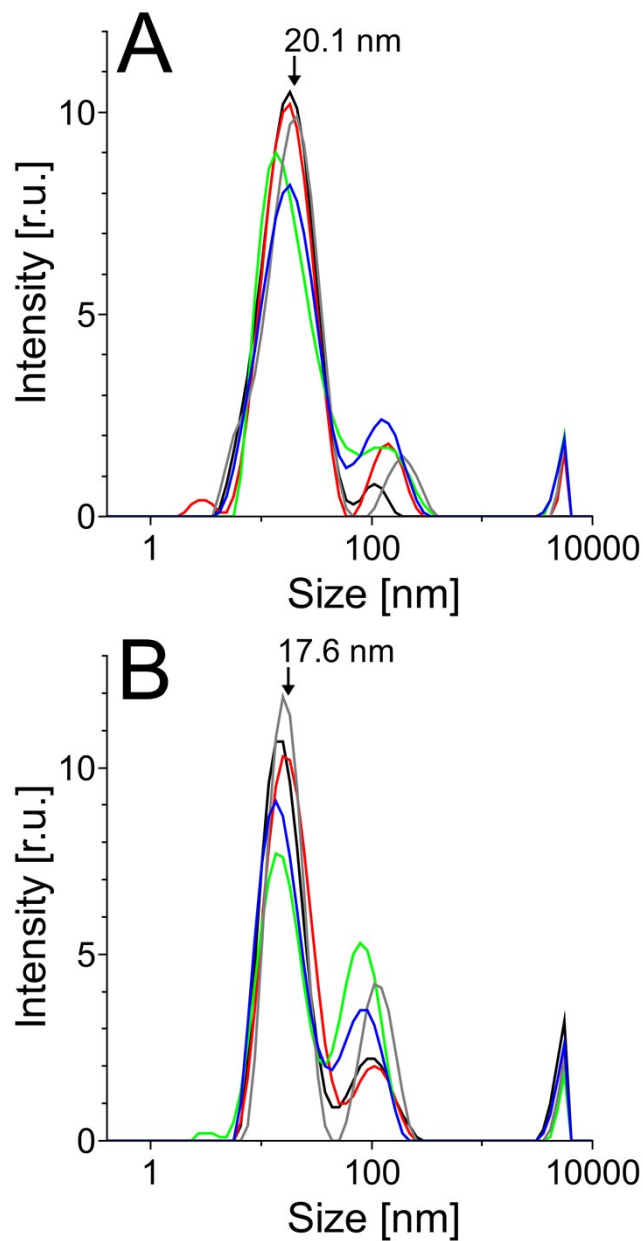
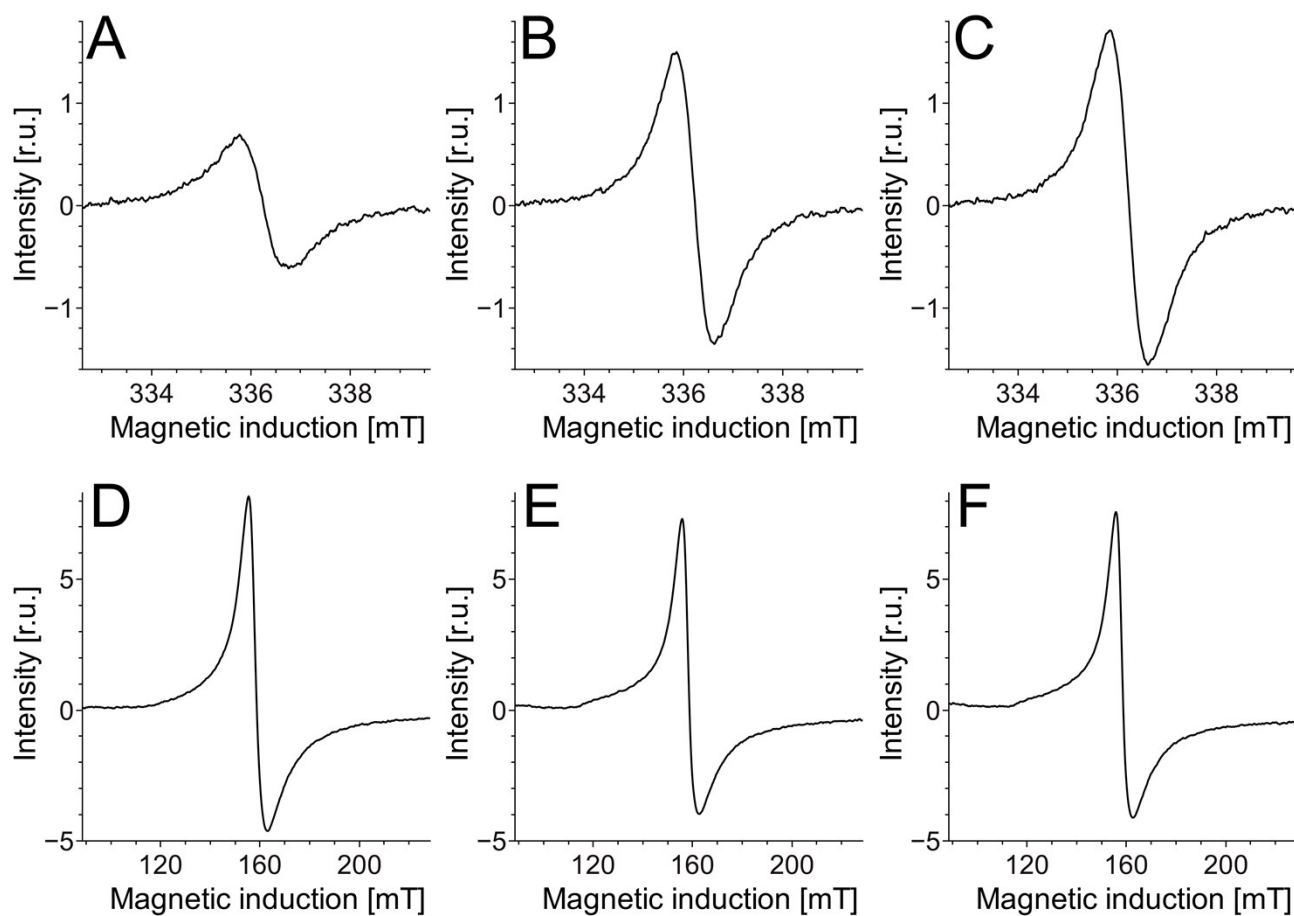


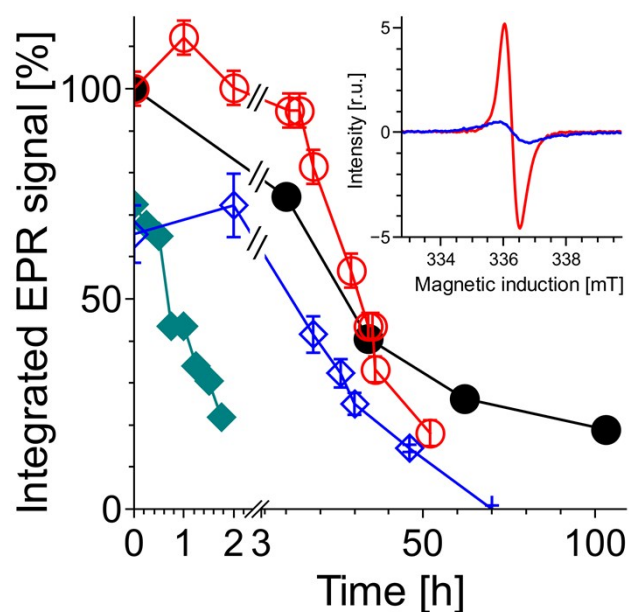
Electronic supplementary information (ESI)



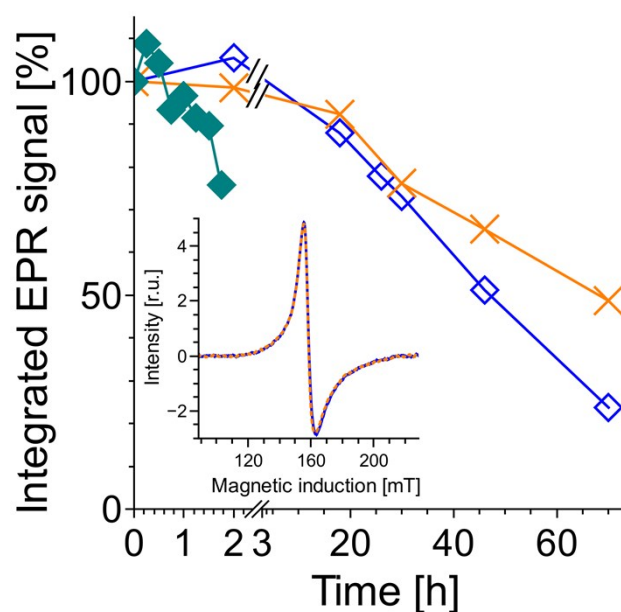
Supplement 1 Size distribution of melanin particle in samples containing 0.1 mg/ml melanin and 400 μ M (A) or 800 μ M (B) potassium ferricyanide.



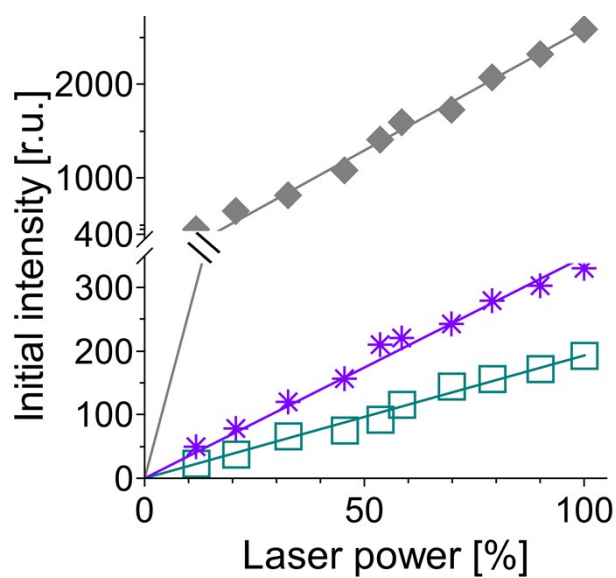
Supplement 2 EPR signal of melanin (A-C) and iron (D-F) in melanin with 1% (w/w) iron in PBS (A,D), 45 mM DTPA adjusted to pH 7.4 (B,E) and 45 mM DTPA with 5 mM KCN, final pH 7.8 (C,F).



Supplement 3. Time-dependent changes of integrated EPR signal of melanin in samples containing melanin without iron (circles) or melanin with 1 % (w/w) iron (diamonds). The samples were incubated with 0.1 M hydrogen peroxide in dark (filled symbols) or irradiated with 400 nm (265 mW/cm²) light without exogenous hydrogen peroxide (open symbols). Inset – EPR spectra of untreated melanin without (red line) or with 1 % (w/w) iron (blue line). The EPR signal was measured at pH 7.4 in PBS. These EPR measurements were carried out at 77 K.



Supplement 4. Time-dependent changes of integrated EPR signal of iron in samples containing melanin with 1 % (w/w) iron incubated with 0.1 M hydrogen peroxide in dark (green filled diamonds) or irradiated with 400 nm (265 mW/cm²) light without exogenous hydrogen peroxide (blue open diamonds and orange crosses). The EPR signal was measured at pH 7.4 in PBS (green filled diamonds and blue open diamonds) or at pH 5 in acetate buffer (orange crosses). Inset – EPR spectra of iron (III) bound to untreated melanin measured at pH 7.4 in PBS (continuous blue line) or at pH 5 in acetate buffer (orange dotted line). These EPR measurements were carried out at 77 K.



Supplement 5. Intensity of singlet oxygen phosphorescence as a function of 405 nm laser pulse energy in samples containing fluorescein (gray filled diamonds), non-degraded melanin without NaN_3 (green open squares) and melanin without NaN_3 degraded for 4 h in phosphate buffer in D_2O (violet stars). The absorbance of these samples was adjusted to 0.108 ± 0.002 .