Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Supporting Information

## Asymmetric sulfoxidation by engineering the heme pocket of a dye-decolorizing peroxidase: An experimental and computational study

Dolores Linde, Marina Cañellas, Cristina Coscolín, Irene Davó-Siguero, Antonio Romero, Fátima Lucas, Francisco J. Ruiz-Dueñas, Victor Guallar and Angel T. Martínez

**Table S1** X-ray data collection and refinement statistics of L357G and F359G variants of *A. auricula-judae* DyP

| | L357G | F359G |
|---|---|---|
| ***Data collection*** | | |
| Beamline | ID23-1 (ESRF) | BL13-XALOC (ALBA) |
| Wavelength (Å) | 0.9792 | 0.9795 |
| Space group | C2 | C2 |
| Unit cell parameters (Å,°) | a=100.9, b=61.0, c=81.0; β=95.0 | a=104.9, b=56.1, c=82.7; β=97.03 |
| Resolution range (Å) | 44.73 - 1.95 (2.05 - 1.95) | 46.63 - 1.10 (1.17 - 1.10) |
| Total reflections | 239,457 (35,489) | 997,210 (135,507) |
| Unique reflections | 35,827 (5,247) | 184,770 (26,363) |
| Multiplicity | 6.7 (6.8) | 5.4 (5.1) |
| Completeness (%) | 99.2 (99.9) | 98.4 (96.4) |
| Mean I/σ(I) | 12.6 (2.3) | 9.5 (2.4) |
| $R_{merge}$[a] | 0.073 (0.729) | 0.088 (0.726) |
| $CC_{1/2}$ (%)[b] | 99.8 (90.2) | 99.7 (77.2) |
| Mosaicity (°) | 0.16 | 0.15 |
| Wilson B factor (Å$^2$) | 33.21 | 7.78 |
| ***Refinement*** | | |
| $R_{work}/R_{free}$ | 0.198 (0.367) / 0.23 (0.415) | 0.149 (0.231) / 0.158 (0.246) |
| Working reflections | 33,925 (5,206) | 182,839 (25,500) |
| Testing reflections | 1,863 (308) | 1,897 (280) |
| Protein atoms (non H) | 3,298 | 3,310 |
| Heme group | 43 | 43 |
| Water molecules | 127 | 576 |
| Mean B factors (Å$^2$): | | |
| -Protein atoms (non H) | 46.2 | 11.9 |
| -Heme group | 41.7 | 7.8 |
| -Water molecules | 47.5 | 24.7 |
| Deviations from ideality: | | |
| -rmsd bond lengths (Å) | 0.007 | 0.006 |
| -rmsd angles (º) | 0.876 | 0.987 |
| Ramachandran statistics: | | |
| -Favoured (%) | 97.5 | 98.9 |
| -Outliers (%) | 0 | 0 |
| PDB code | 5IKG | 5IKD |

Statistics for the highest-resolution shell are shown in parenthesis. [a]$R_{merge} = \Sigma_{hkl}\Sigma_i |I_i(hkl) - \langle I(hkl)\rangle| / \Sigma_{hkl}\Sigma_i I_i(hkl)$, where $I_i(hkl)$ is the intensity measured for the *i*th reflection and $\langle I(hkl)\rangle$ is the average intensity of all reflections with indices *hkl*. [b]$CC_{1/2}$ is the correlation coefficient between two random half datasets (Karplus P.A and Diederichs K., Science, 2012, 336, 1030-1033).

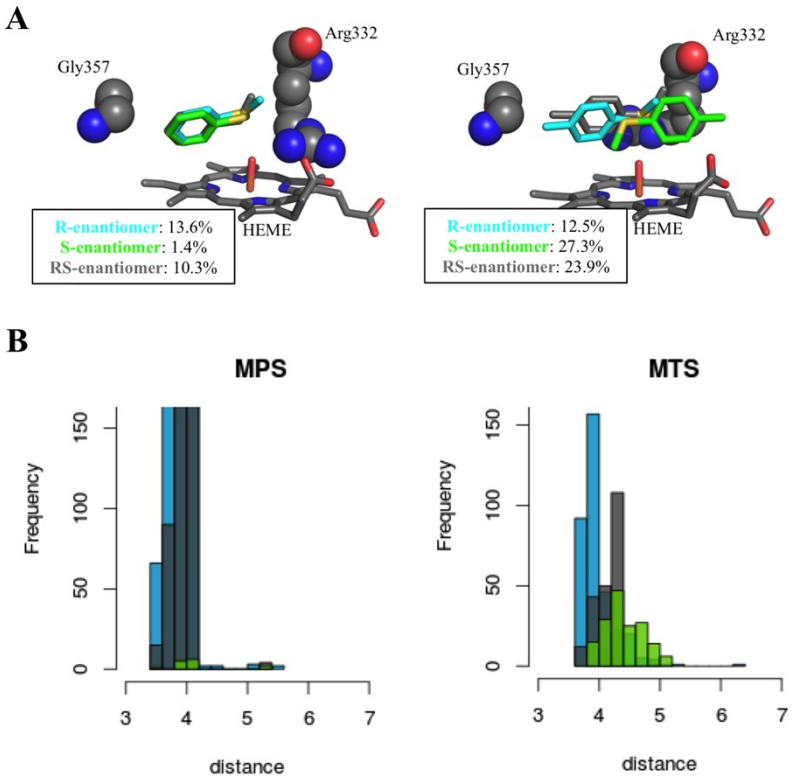


**Fig. S1.** L357G variant substrate oxidation and positioning analysis: **A)** pro-*R*, pro-*S* and pro-*RS* MPS (left) and MTS (right) positioning on the L357G variant. Spin density population on the substrate, from QM/MM calculations, is indicated in each image. **B)** Frequency distance (in Å) distribution of MPS and MTS S atom to Arg332 CZ atom in the L357G variant for the selected reactive structures: last 10 kcal·mol$^{-1}$ interaction energies and distances to the heme group below 5 Å. Pro-*S* substrate positions are colored in green, pro-*R* in cyan and pro-*RS* in gray.

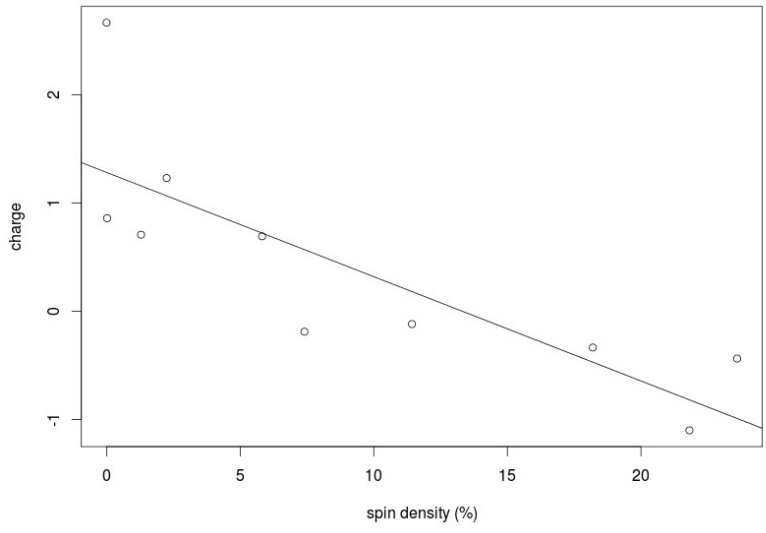


**Fig. S2.** Correlation between the substrate spin density and the charge distribution on 10 representative points.