Electronic supplementary information

# Direct synthesis of phenol by novel [FeFe]-hydrogenase model complexes as catalysts of benzene hydroxylation with $H_2O_2$

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**Table S1** Selected bond lengths (Å) and bond angles(°) for complexes **1-3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Fe(1)-Fe(2) | 2.5054(7) | 2.5090(4) | 2.5126(11) |
| Fe(1)-S(1) | 2.2481(10) | 2.2669(5) | 2.2629(19) |
| Fe(1)-S(2) | 2.2213(10) | 2.2700(5) | 2.225(2) |
| Fe(2)-S(1) | 2.2457(9) | 2.2792(5) | 2.304(2) |
| Fe(2)-S(2) | 2.2571(10) | 2.2514(5) | 2.2510(19) |
| Fe(1)-P(1) | | 2.2734(5) | 2.2447(15) |
| S(1)-Fe(1)-Fe(2) | 56.07(3) | 56.739(13 | 57.42(6) |
| S(1)-Fe(2)-Fe(1) | 56.16(3) | 56.268(14) | 55.84(5) |
| S(2)-Fe(1)-Fe(2) | 56.66(3) | 55.943(12) | 56.34(6) |
| S(2)-Fe(2)-Fe(1) | 55.31(3) | 56.650(14) | 55.36(6) |
| P(1)-Fe(1)-Fe(2) | | 158.008(15) | 154.76(5) |

**Table S2** Crystallographic data and refinement parameters for complexes **1-3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{10}H_8Fe_2O_6S_2$ | $C_{27}H_{41}Fe_2O_5PS_2$ | $C_{27}H_{23}Fe_2O_5PS_2$ |
| Formula weight | 399.98 | 652.39 | 634.24 |
| Space group | P-1 | P2(1)/n | P-1 |
| T (K) | 113(2)K | 113(2)K | 113(2) K |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal size (mm) | 0.20 x 0.18 x 0.12 | 0.20 x 0.18 x 0.12 | 0.20 x 0.12 x 0.11 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| *a* (Å) | 9.4793(11) | 13.8434(14) | 9.846(2) |
| *b* (Å) | 11.1920(11) | 12.6809(14) | 11.197(2) |
| *c* (Å) | 15.6287(15) | 17.600(2) | 13.562(2) |
| $\alpha$ (º) | 91.4370(10) | 90 | 96.013(3) |
| $\beta$ (º) | 101.320(2) | 102.580 | 93.089(4) |
| $\gamma$ (º) | 113.660(2) | 90 | 111.076(5) |
| V (Å$^3$) | 1479.2(3) | 3015.4(6) | 1380.8(5) |
| Z | 4 | 4 | 2 |
| $\rho$ (g/cm$^3$) | 1.796 | 1.437 | 1.525 |
| $\theta$ range (º) | 3.01-27.52 | 3.02 - 27.53 | 3.04-25.02 |
| $\mu$ (mm$^{-1}$) | 2.260 | 1.188 | 1.295 |
| F(000) | 800 | 1368 | 648 |
| goodness-of-fit on $F^2$ | 1.018 | 1.057 | 1.076 |
| $R$ [$I \geq 2\sigma(I)$] | 0.0450, wR2 = 0.1063 | 0.0286, wR2 = 0.0715 | 0.0618, wR2 = 0.1701 |
| $R$ (all data) | 0.0482, wR2 = 0.1083 | 0.0298, wR2 = 0.0722 | 0.0642, wR2 = 0.1749 |

**Table S3** Catalytic hydroxylation of benzene to phenol with different oxidants in the presence of complex **1**. [a]

| Entry | Oxidant | Yield [%] | Selectivity [b] [%] |
|---|---|---|---|
| 1 | *m*-CPBA | 4.2 | 94 |
| 2 | $O_2$ | 0 | 0 |
| 3 | $H_2O_2$ | 12.6 | 85 |
| 4 | PhIO | 0 | 0 |

[a] 1, 30 μmol; 60 °C; benzene, 0.1 mL; $CH_3CN$, 2.0 mL; oxidants, 5.0 mmol; reaction time, 3 h. [b] Selectivity: yield of phenol/benzene conversion.