Supplementary Information

Insights into the Catalytic Mechanism of Chlorophenol 4-Monooxygenase: A Quantum Mechanics/Molecular Mechanics Study

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Keywords
Catalytic mechanism, Polychlorinated phenols, Electrostatic influence, Quantum mechanical/molecular mechanical method

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Table S1 Dependency of the energy barriers on the QM size, the smaller QM region (98 atoms) contains oxidation state of co-enzyme FADHOOH, functional groups of residues Arg100, Phe153, Val154, Thr192, His289 and the substrate 2,4,5-TCP, the larger QM region (212 atoms) contains additional residues such as Ala104, Pro150, Leu151, Glu251, Phe285, Cal288, Arg295, Arg366, and Phe442.

Figure S1 The optimized structures at B3LYP/6-31G(d,p) level and calculated energies at B3LYP/6-311++G(d,p) level by using Gaussian program. Energies are given in kcal mol$^{-1}$. A and C are two possible conformations of 5-Cl-2-H-BQ while B and D are two possible conformations of 4-Cl-3-H-BQ (P-10).

Figure S2 Optimized reactant (R’-1), transition state (TS’-2), and intermediate (IM’-3) structures for the hydroxylation step of TftD towards 2,4,6-TCP at B3LYP/6-31G(d,p)//CHARMM22 level. The unit of the bond distances and imaginary frequency are in Å and cm$^{-1}$.

Figure S3 Optimized reactant (R-6), transition state (TS-7), and intermediate (IM-8) structures for the hydroxylation step of TftD towards 2,5-DiCHQ at B3LYP/6-31G(d,p)//CHARMM22 level. The unit of the bond distances and imaginary frequency are in Å and cm$^{-1}$.
Table S1: Dependency of the energy barriers on the QM size, the smaller QM region (98 atoms) contains oxidation state of co-enzyme FADHOOH, functional groups of residues Arg100, Phe153, Val154, Thr192, His289 and the substrate 2,4,5-TCP, the larger QM-region (212 atoms) contains additional residues such as Ala104, Pro150, Leu151, Glu251, Phe285, Cal288, Arg295, Arg366, and Phe442.

<table>
<thead>
<tr>
<th>Snapshots</th>
<th>Energy barriers/(kcal mol⁻¹)</th>
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<tr>
<td></td>
<td>Smaller QM-region</td>
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<tr>
<td>3 ns</td>
<td>16.3</td>
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<td>4 ns</td>
<td>18.2</td>
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<td>5 ns</td>
<td>24.7</td>
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Figure S1
Figure S2
Figure S3