Supplementary Information

Effect of toxic ligands on O_2 binding to heme and their toxicity mechanism

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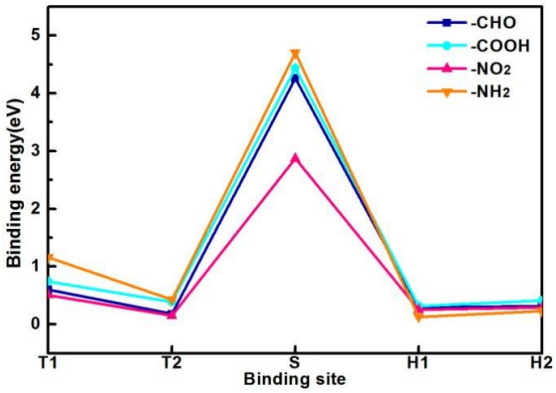

Fig.S1. Binding energy of funtional groups bound to heme at considered binding sites

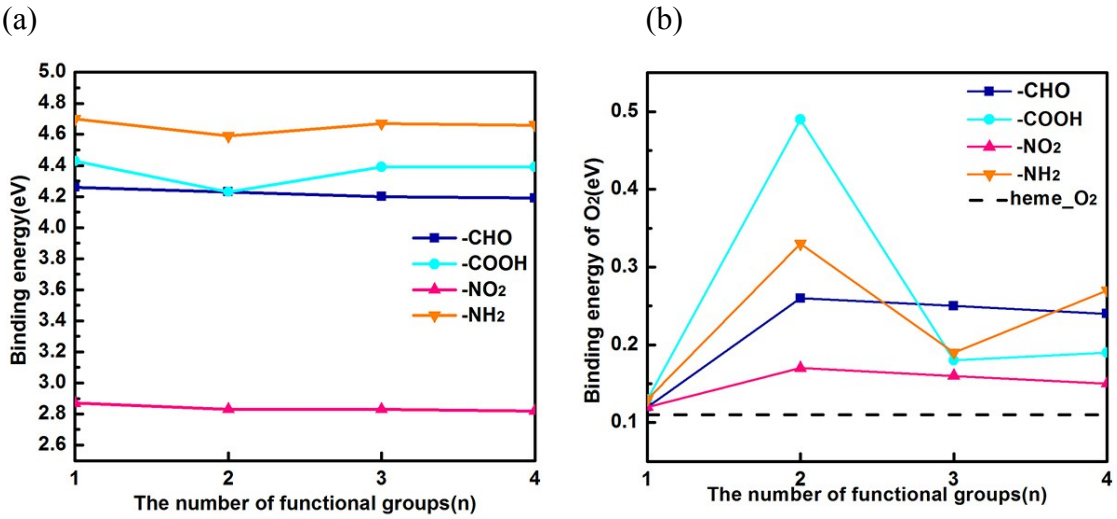

Fig.S2. (a) The tendency of the binding energy of functional groups to change over the number of functional groups bound at the side (Ss) of heme. (b) The binding energy of O_2 on the top site of

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the Fe center versus the number of functional groups bound at the side (Ss) of heme and the black dash line represents the O_2 binding energy in the oxyheme system.

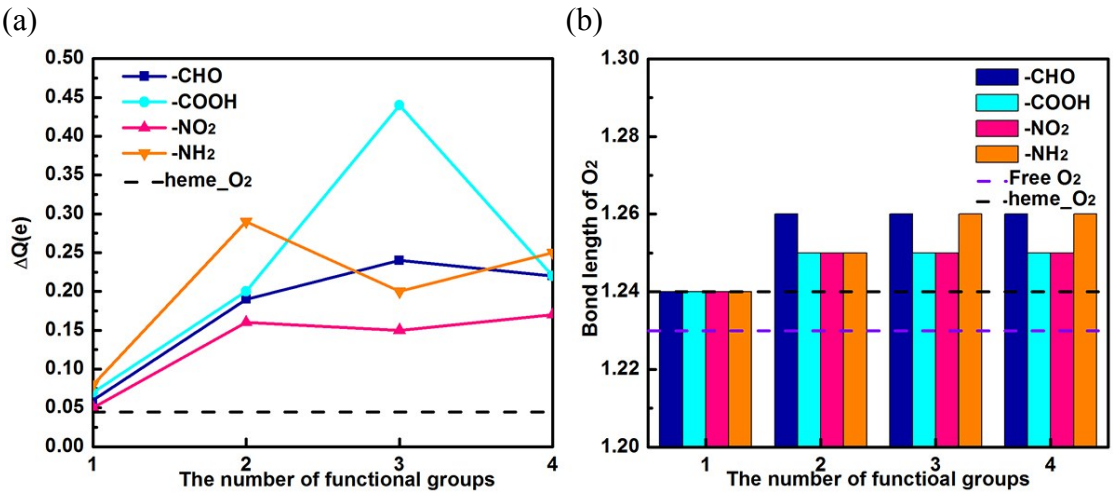

Fig.S3. (a) The number of electrons obtained by O_2 varies with the number of functional groups bound to heme side site (Ss) and the parallel dotted line represents the number of electrons gained by O_2 in oxyheme system. (b) The bond lengths of O_2 bound to the top of Fe atom (T1) changes with the number of functional groups connected to heme side (Ss), where parallel purple and black dash lines represent the bond lengths of O_2 in free state and oxyheme system, respectively.

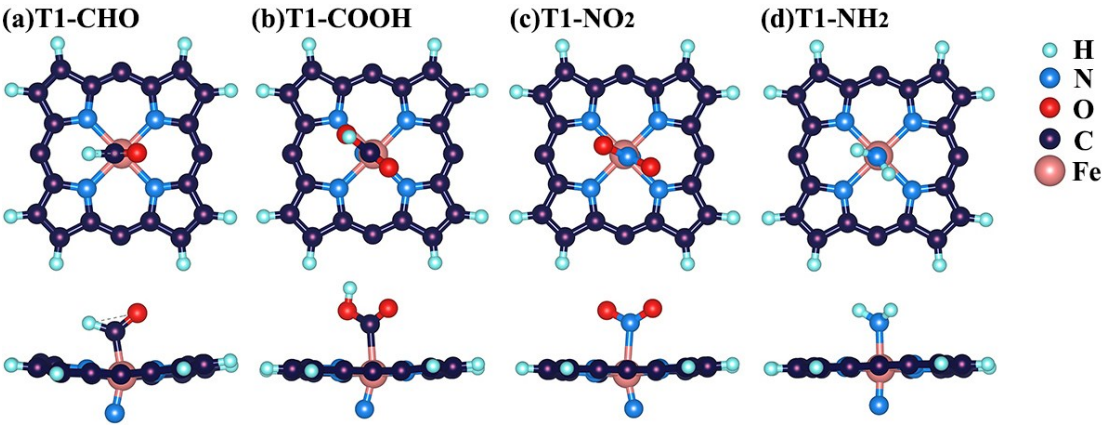

Fig.S4. Optimized geometries of bound functional groups (a)-CHO, (b)-COOH, (c)-NO_2, (d)-NH_2 on heme at top site (T1) of the Fe atom.

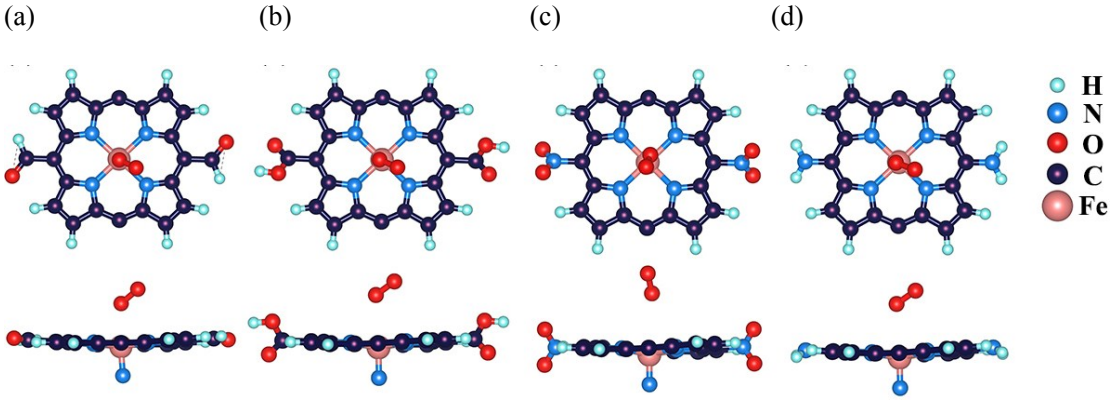

Fig.S5. Optimized geometries of bound functional groups (a) -CHO, (b) -COOH, (c) -NO_2, (d) -NH_2 on oxyheme at side (Ss) site.

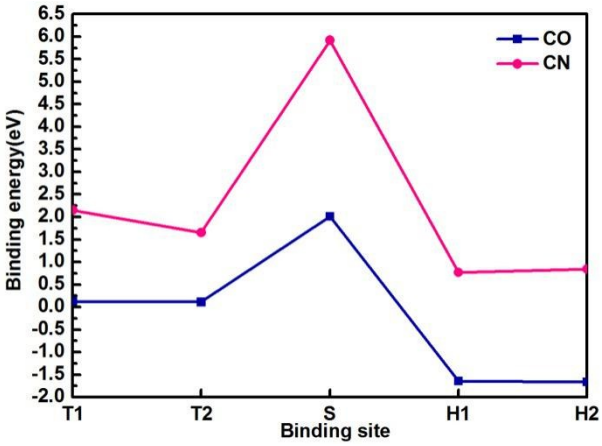

Fig.S6. Binding energy of CO, CN bound to heme at various binding sites

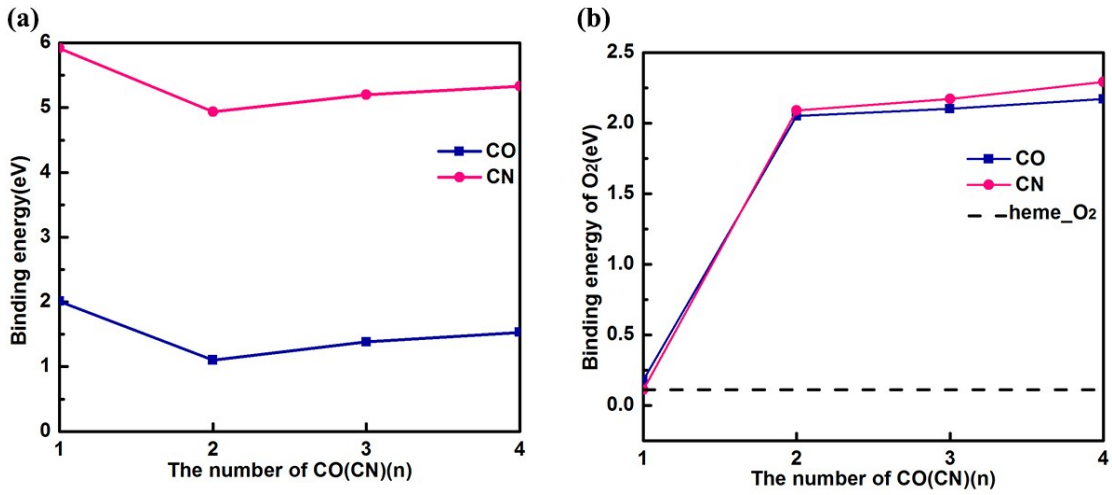

Fig.S7. (a) The tendency of the binding energy of CO (CN) to change over the number of CO (CN) bound at the side (Ss) of heme. (b) The binding energy of O_2 on the top site of the Fe center versus

the number of CO (CN) bound at the side (Ss) of heme and the black dash line represents the O_2 binding energy in the oxyheme system.

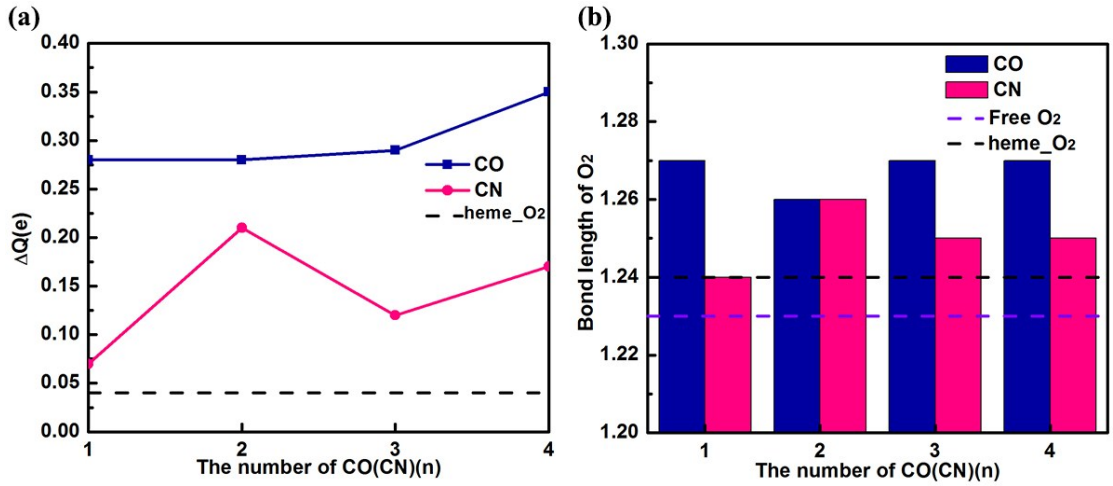

Fig.S8. (a) The number of electrons gained by O_2 varies with the number of CO and CN bound to heme side site (Ss) and the parallel dotted line represents the number of electrons gained by O_2 in oxyheme system. (b) The bond lengths of O_2 bound to the top of Fe atom (T1) changes with the number of CO and CN connected to heme side (Ss), where parallel purple and black dash lines represent the bond lengths of O_2 in free state and oxyheme system, respectively.

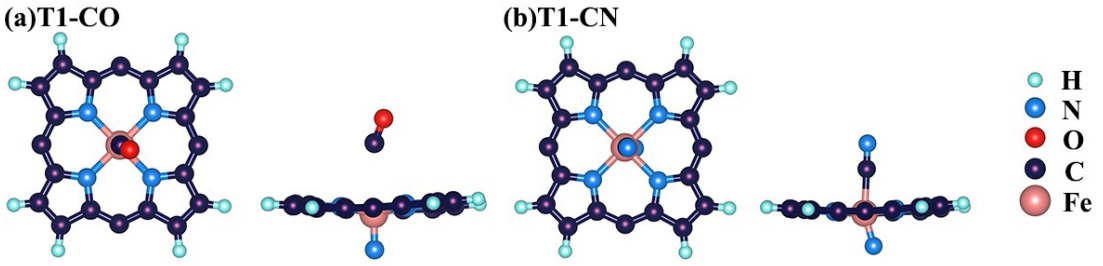

Fig.S9. Optimized geometries of (a) CO, (b) CN at top site (T1) of the Fe atom.

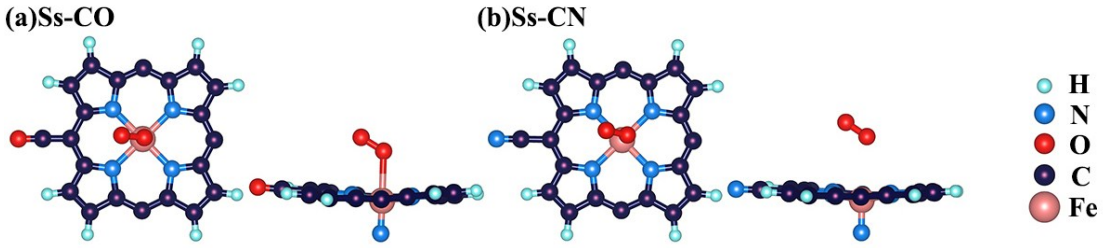

Fig.S10. Optimized geometries of (a) CO, (b) CN on oxyheme at side (Ss) site.

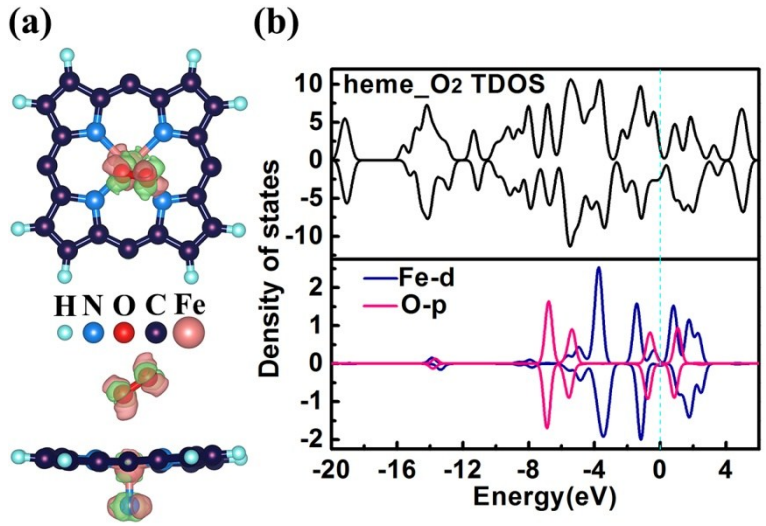

Fig.S11. (a) Charge density difference (CDD) of the heme_O_2 system and the isosurface value is taken as 0.003 eÅ^{-3}. The green and red regions stand for the charge reduction and accumulation. (b) TDOS, PDOS of the heme_O_2 system, the Fe atom and proximal O atom of O_2, and the Fermi level is indicated by vertical dash lines.

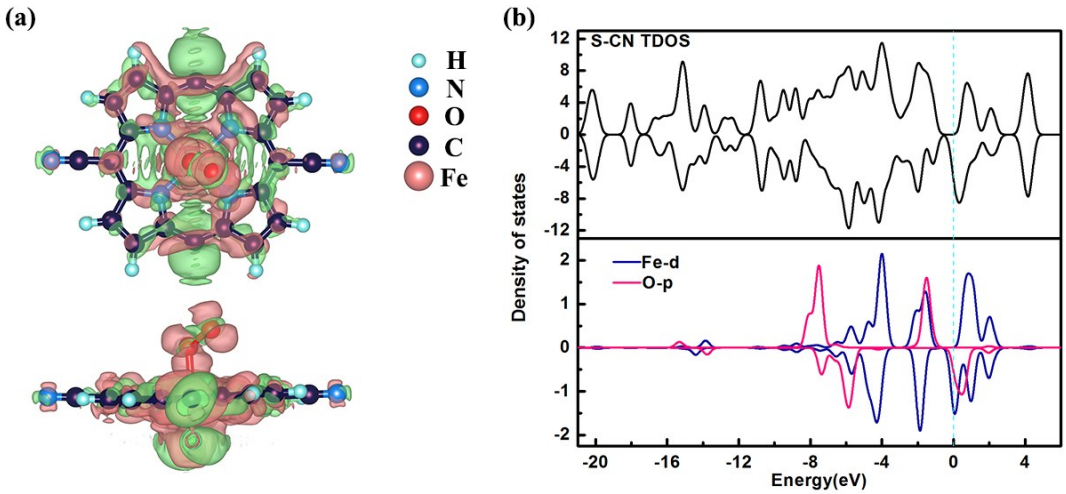

Fig.S12. CDD and DOS of the oxyheme sytem with two CN bound to heme at side site (Ss). The isosurface value is taken as 0.001 eÅ^{-3}. The green and red regions stand for the charge reduction and accumulation. The Fermi level is indicated by vertical dash lines.

Table S1 The calculated parameters of various ligands bound to heme at T1 site. E_b (eV), binding energy of ligands. ΔQ (e), electrons transfer between heme and ligands, and the positive value indicates that ligands gain electrons.

T1	O_2	-CHO	-COOH	$-NO_2$	$-NH_2$	CO	CN
E_b(eV)	0.11	0.60	0.74	0.51	1.16	0.13	2.15
ΔQ(e)	0.04	-0.11	0.33	0.49	0.32	0.03	0.54

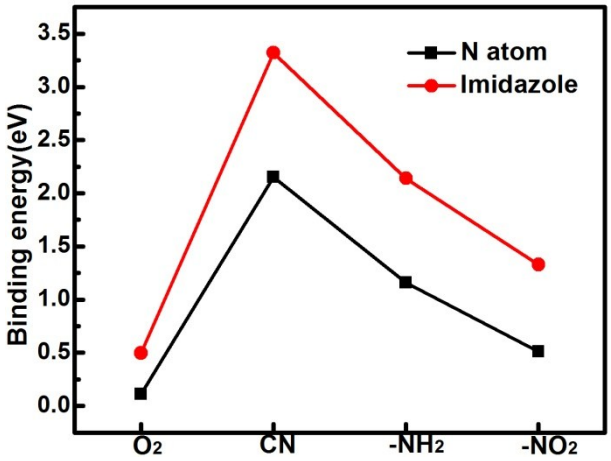

Fig.S13. Binding energies of ligands (O_2, CN, $-NH_2$ and-NO_2) bound to our heme model (a N atom as the fifth ligand of the Fe atom in the axial position) and FePIm system (the deoxy-Fe porphyrin system with an axial imidazole ligand), respectively.

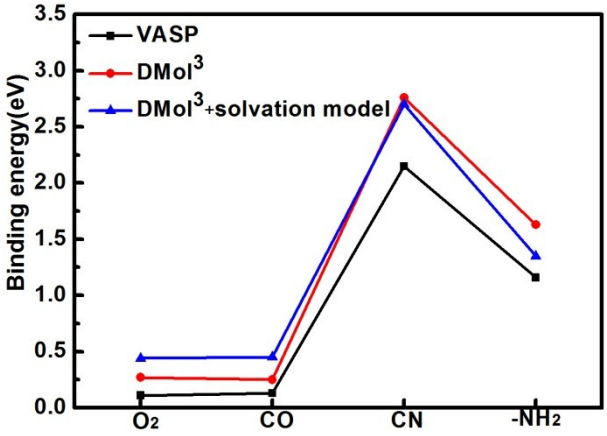

Fig.S14. Binding energies of ligands (O_2, CO, CN and $-NH_2$) bound to heme at T1 site are calculated by VASP and $DMol^3$ codes, respectively.