

Supplementary Materials

Spectroscopic study and electronic structure of prototypical iron porphyrins and their μ -oxo-dimer derivatives with different functional configurations

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I. Model structure

Table S1 Crystal structure information of the four investigated porphyrins

Compounds	Formula and name	Space group	Unit Cell (Å)	Unit Cell Angles (°)	Coordinate of Fe
Porphyrin-1	$C_{34}H_{32}Cl_1Fe_1N_4O_4$ [Fe-PPIX-Cl]	P1 (No.2)	a=11.494 b= 4.097 c=10.854	$\alpha= 98.56$ $\beta=108.48$ $\gamma=107.65$	4Fe-N ~ 2.1 Å Fe-Cl ~ 2.2 Å
Porphyrin-2	$C_{72}H_{72}Fe_2N_8O_9$ [μ -oxo-dimer-Fe-PPIX]	P1 (No.2)	a= 8.949 b=15.168 c=24.860	$\alpha=107.51$ $\beta=91.60$ $\gamma=100.45$	1Fe-O ~ 1.8 Å 4Fe-N ~ 2.1 Å
Porphyrin-3	$C_{44}H_{28}Cl_1Fe_1N_4$ [Fe-TPP-Cl]	P 2 ₁ /n (No.14)	a=10.254 b=15.969 c=20.810	$\alpha= 90$ $\beta= 90.48$ $\gamma= 90$	4Fe-N ~ 2.1 Å Fe-Cl ~ 2.2 Å
Porphyrin-4	$C_{88}H_{56}Fe_2N_8O_1$ [μ -oxo-dimer-Fe-TPP]	C 2cb (No.41)	a=15.094 b=24.938 c=17.825	$\alpha= 90$ $\beta= 90$ $\gamma= 90$	1Fe-O ~ 1.8 Å 4Fe-N ~ 2.1 Å

II. Photoreduction effects:

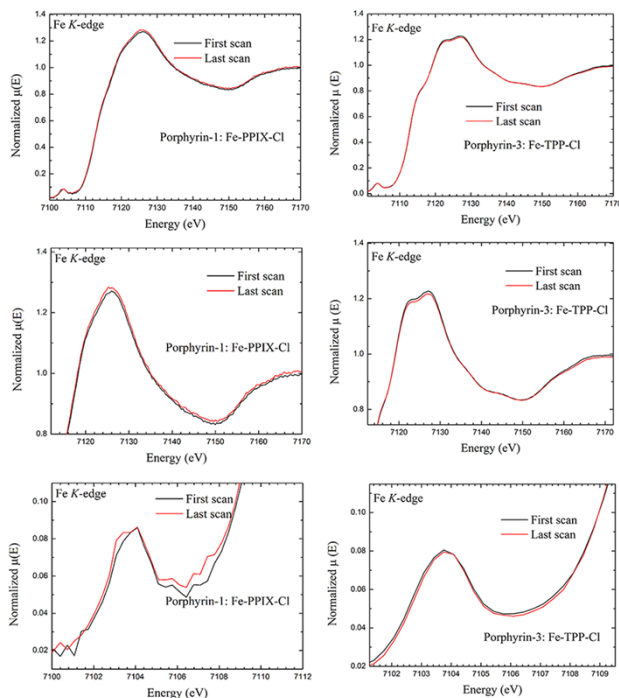


Figure.S1 Comparison of the first and last scanned Fe K-edge XANES spectra of porphyrin-1 (left panel): the Fe-PPIX-Cl; and of porphyrin-3 (right panel): the Fe-TPP-Cl. The Fe-PPIX-Cl was exposed for four minutes after the first opening of the shutter for four consecutive scans (each takes ~ 120 second) while the Fe-TPP-Cl was exposed for two hours. After X-ray irradiation both show no spectral differences within the signal to noise ratio.

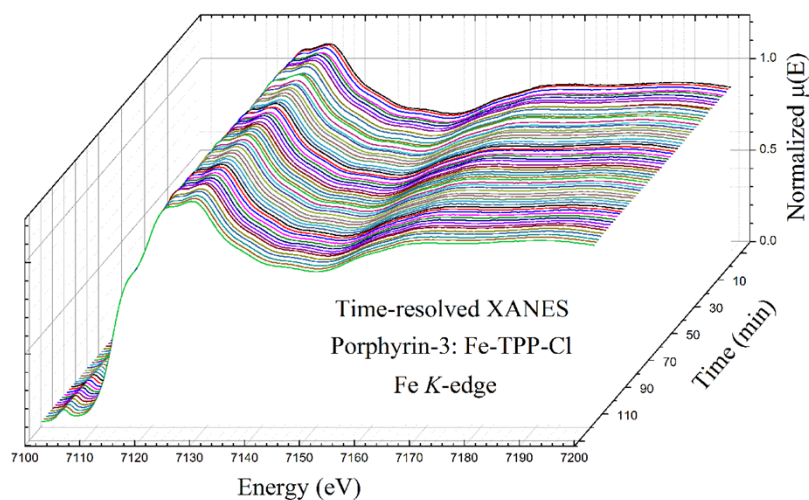


Figure.S2 Time-resolved Fe K-edge XANES spectra of the Porphyrin-3: the Fe-TPP-Cl. The normalized XANES spectra show again no detectable spectral differences after two hours of continuous X-ray irradiation with the unfocused beam at the bending magnet beamline B18 at Diamond.

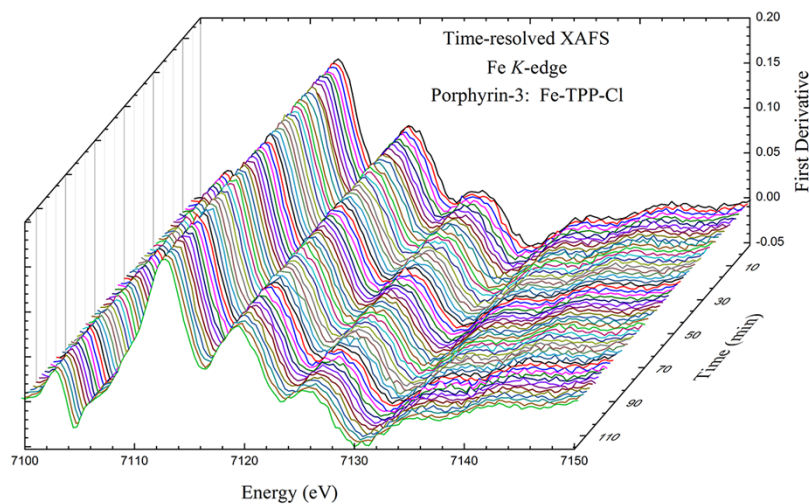


Figure.S3 First derivative of the time-resolved Fe K-edge XANES spectra of the porphyrin-3: the Fe-TPP-Cl. Also the derivative spectra show no detectable differences after two hours of continuous X-ray irradiation with the unfocused beam at the bending magnet beamline B18 at Diamond.

III. Electronic structure calculations

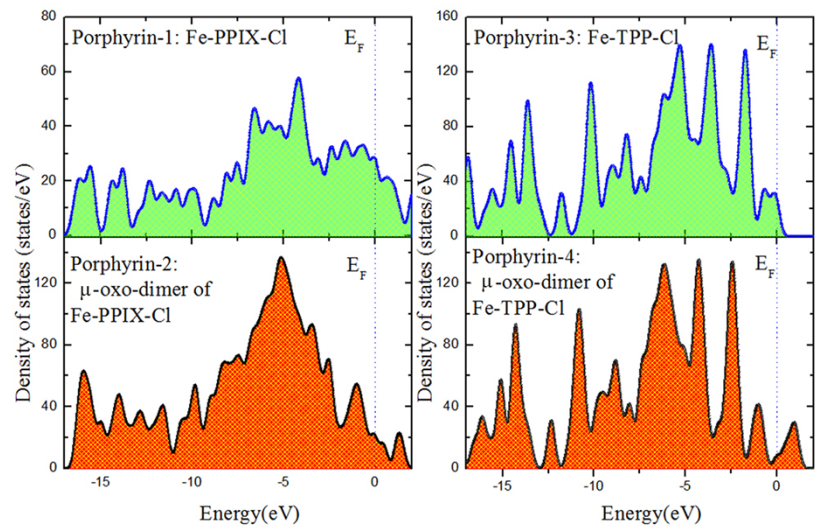


Figure.S4 Comparison of the total density of electronic states of the four Fe-porphyrins.

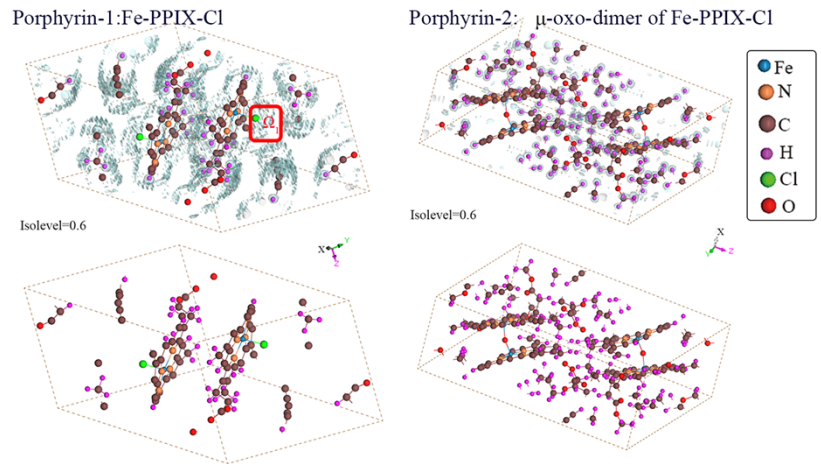


Figure. S5 Porphyrin-1 vs. porphyrin-2: the 3d isosurface plot of the electron localization function with the isosurface set to 0.6. Ω_1 is the localization of electron pairs near the Cl atoms.

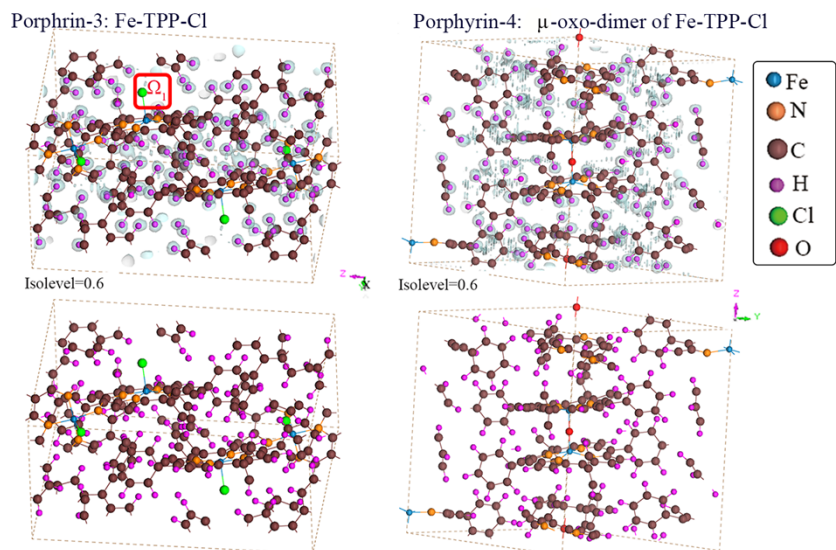


Figure. S6 Porphyrin-3 vs. porphyrin-4: the 3d isosurface plot of the electron localization function with the isosurface level set to 0.6. Ω_1 is the localization of electron pairs near the Cl atoms.

IV. Charge transfer parameters

Table.S2 Charge transfers of different atoms in the four porphyrin complexes.

Charge transfer	Porphyrin-1	Porphyrin-2	Porphyrin-3	Porphyrin-4
Fe	-0.162	-0.067	-0.131	-0.076
C	-0.064	-0.129	-0.057	-0.058
H	0.164	0.149	0.083	0.098
N	-0.046	-0.072	-0.017	-0.038
O	-0.148	-0.127	0	-0.092
Cl	0.202	0	0.248	0