Supporting Information

Table S1: Crystallization Conditions from Screening for *Ne c*-552r

Condition	*Precipitant*	*Salt*	*Buffer*
JCSG I-2	20% (*w/v*) PEG 6000		0.1 M Bicine pH 8.5
JCSG I-23	20% (*w/v*) PEG 3350	0.2 M Na-formate	
JCSG I-94	20% (*w/v*) PEG 6000	1.0 M LiCl	0.1M citric acid pH 4.0
JCSG II-17	20% (*w/v*) PEG 6000	1.0 M LiCl	0.1 M TRIS pH 8.5
JCSG III-4	30% (*w/v*) PEG 3000		0.1 M CHES pH 9.0
JCSG III-43	20% (*w/v*) PEG 6000	1.0 M LiCl	0.1 M HEPES pH 7.0
Index-2	2.0 M $(NH_4)_2SO_4$		0.1 M $NaCH_3COO$ pH 4.5
JCSG+-1	50% PEG 400	0.2 M Li_2SO_4	0.1 M $NaCH_3COO$ pH 4.5
SIGMA-1	1.4 M $NaCH_3COO$		0.1 M Na cacodylate pH 6.5
SIGMA-20	30% PEG 4000	0.2 M $(NH_4)_2SO_4$	0.1 M $NaCH_3COO$ pH 4.6

Table S2: Crystallization Conditions from Screening for *Ne* N64Δ

Condition	*Precipitant*	*Salt*	*Buffer*
JCSG I-1	20% (*w/v*) PEG 8000		0.1M CHES pH 9.5
JCSG I-2	20% (*w/v*) PEG 6000		0.1 M Bicine pH 8.5
JCSG II-15	20% (*w/v*) PEG 8000	0.2 M $Ca(CH_3COO)_2$	0.1 M Imidazole pH 8.0
JCSG II-18	20% (*w/v*) PEG 6000		0.1M TRIS pH 8.5
JCSG II-90	10% (*w/v*) PEG 1000 10% (*w/v*) PEG 8000		
JCSG III-20	10% (*w/v*) PEG 3000	0.2 M Li_2SO_4	0.1 M Imidazole pH 8.0
JCSG III-22	2.4 M $(NH_4)_2SO_4$		0.1M TRIS pH 8.5
JCSG III-37	1.0 M Na/K tartrate	0.2 M NaCl	0.1 M Imidazole pH 8.0
JCSG IV-32	1.0 M di-ammonium phosphate	0.2 M NaCl	0.1 M Imidazole pH 8.0

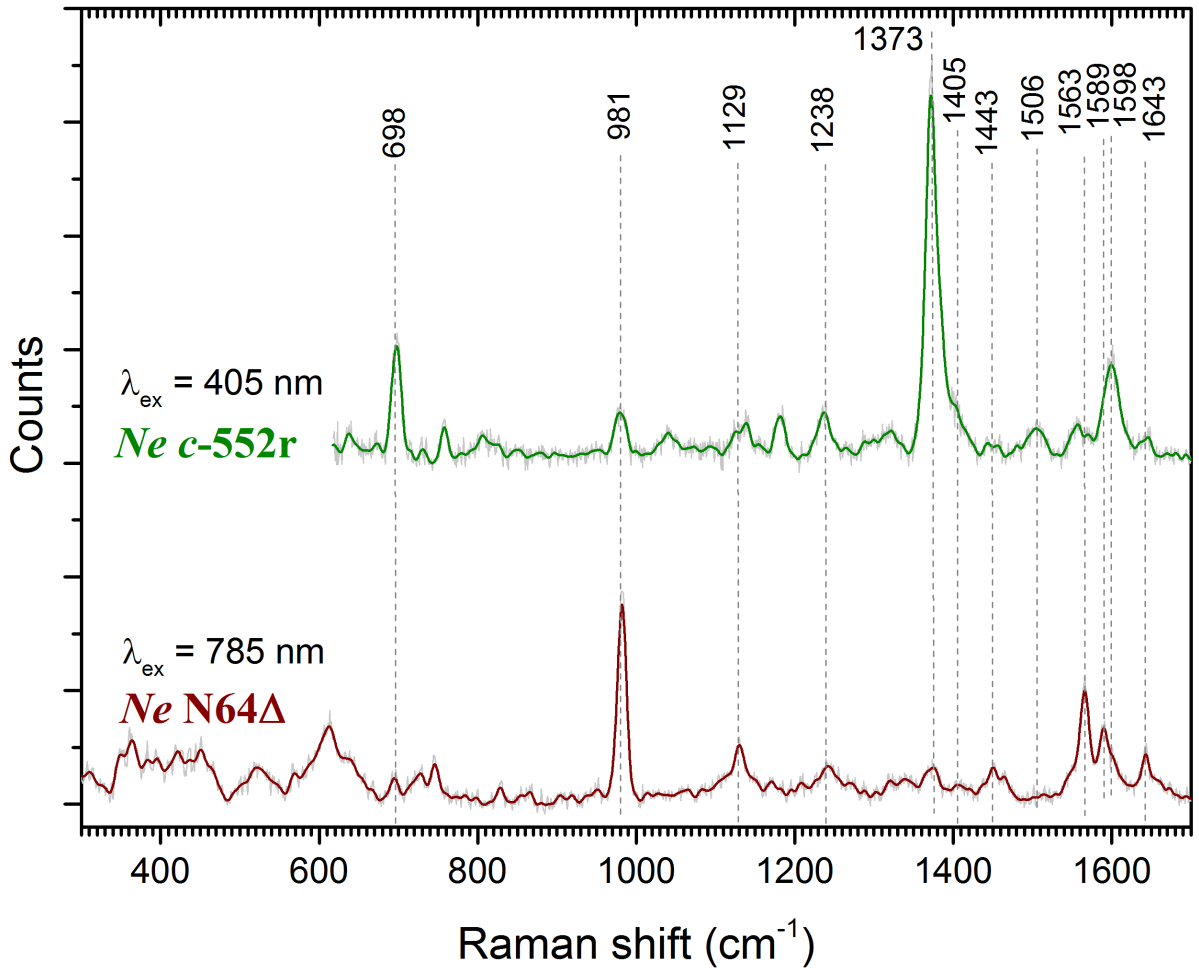

Figure S1. Single-crystal resonance Raman spectra of oxidized *Ne c*-552r (green) and Raman spectra of oxidized *Ne* N64Δ (red) before exposure to X-rays. Excitation wavelength for *Ne c*-552r and *Ne* N64Δ was 405 and 785 nm, respectively. The un-smoothed spectra are shown in grey.

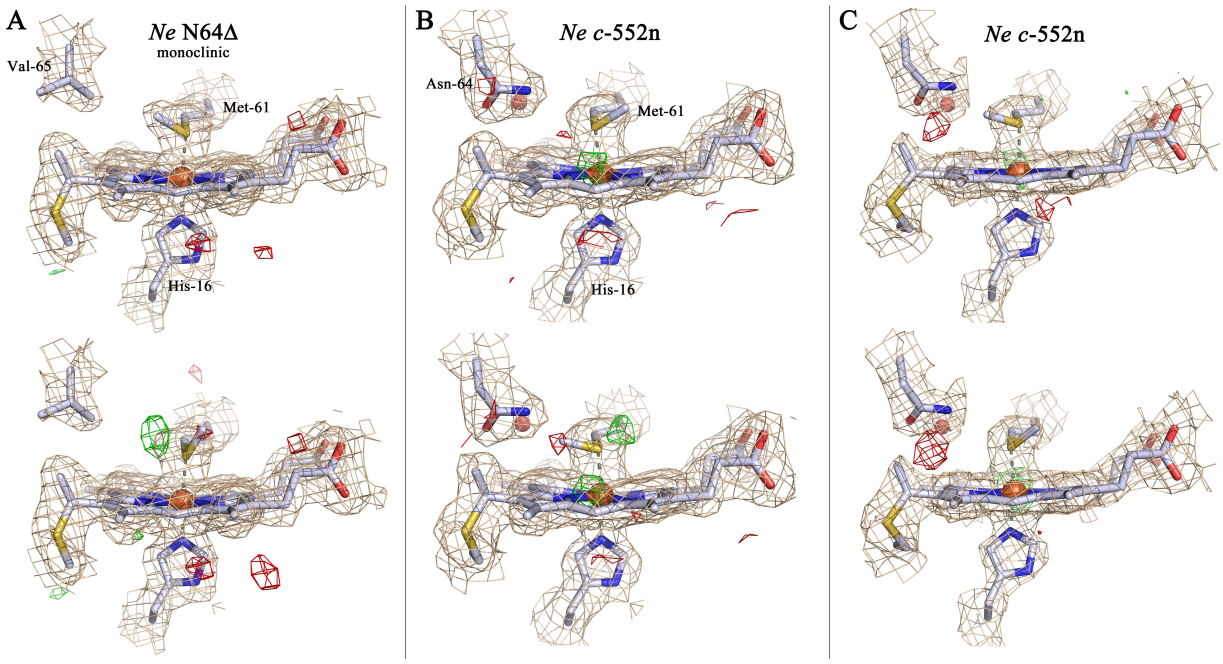

Figure S2. Structures and electron density maps of *Ne* N64Δ (A) and *Ne c*-552n (two monomers with different Met orientation) (B,C) after refining with both *R* or *S* configuration of the sulfur Met-61 residue. The upper structures show the Met orientation for the published structures. The lower structures show the electron density after re-refining in the opposite Met orientation. The $2F_o$-F_c electron density maps (wheat) are shown at 1σ, while the F_o-F_c electron density difference maps are contoured at +3σ (green) and -3σ (red).

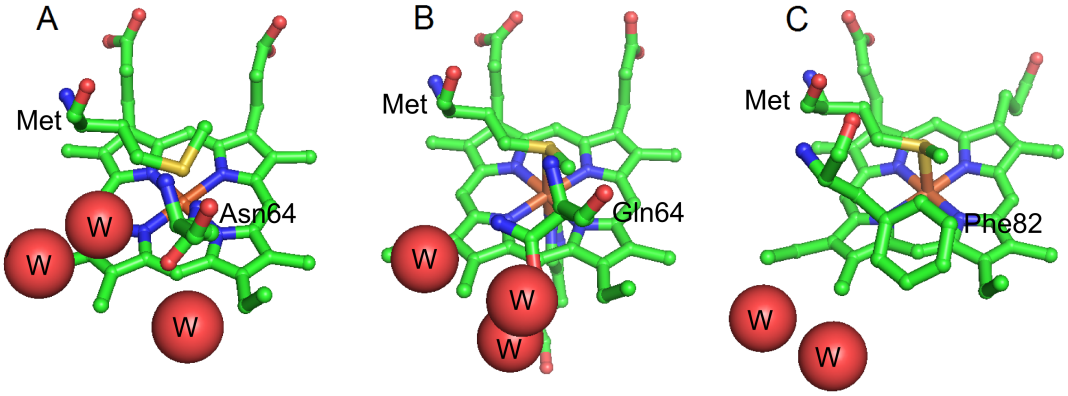

Figure S3. Residues and the water molecules (red spheres) near the heme and the axial Met for A) *Pa c*-551 (351C), B) *Ht c*-552 (1YNR), and C) horse cyt *c* (1HRC).