Two-dimensional ^{67}Zn HYSCORE spectroscopy reveals that a Zn-Bacteriochlorophyll a_P' dimer is the primary donor (P_{840}) in the Type-1 reaction centers of *Chloracidobacterium thermophilum*

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SUPPLEMENTARY INFORMATION

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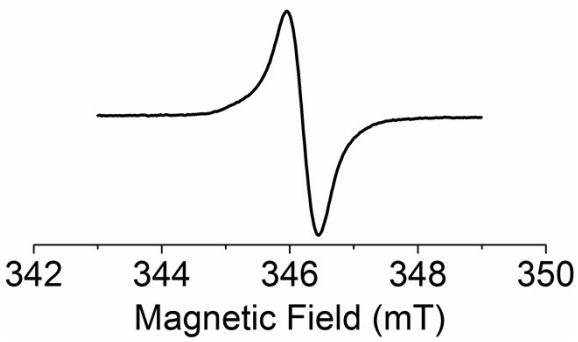

Figure 1S. Continuous-wave EPR spectrum of the Zn^{2+}-protoporphyrin IX cation at 50 K. The spectrum displays a signal at g = 2.003. The cationic species was generated by cryogenic white light illumination of a 6 mM Zn^{2+}-protoporphyrin IX using ACN as a solvent.

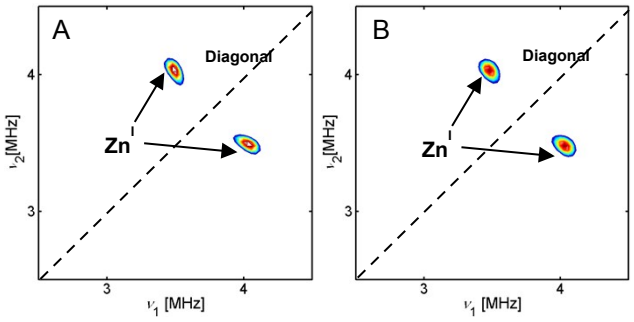

Figure 2S. **(A)** Experimental and **(B)** simulated 2D ^{67}Zn HYSCORE spectrum of the Zn^{2+}-protoporphyrin IX cation at 5 K. The spectrum displays a pair of cross-peaks that are symmetric about the main diagonal that arise from the magnetic interaction of ^{67}Zn (nuclear spin, I = 5/2) with the unpaired electron spin (S = ½) of the Zn^{2+}-protoporphyrin IX cation.

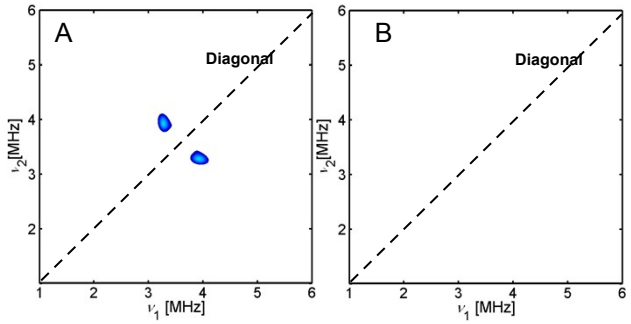

Figure 3S. Comparison of the experimental 2D ^{67}Zn HYSCORE spectrum of **(A)** ^{67}Zn-labelled and **(B)** unlabelled *C. thermophilum* membranes containing RCs. Both of the plots are normalized by the same number of scans on samples with similar concentrations. The cross-peaks from the hyperfine interactions with the ^{67}Zn atom(s) that are observed in part (A) are a result of the high levels of isotopic enrichment of ^{67}Zn in the ^{67}Zn-labelled *C. thermophilum* membranes containing RCs.

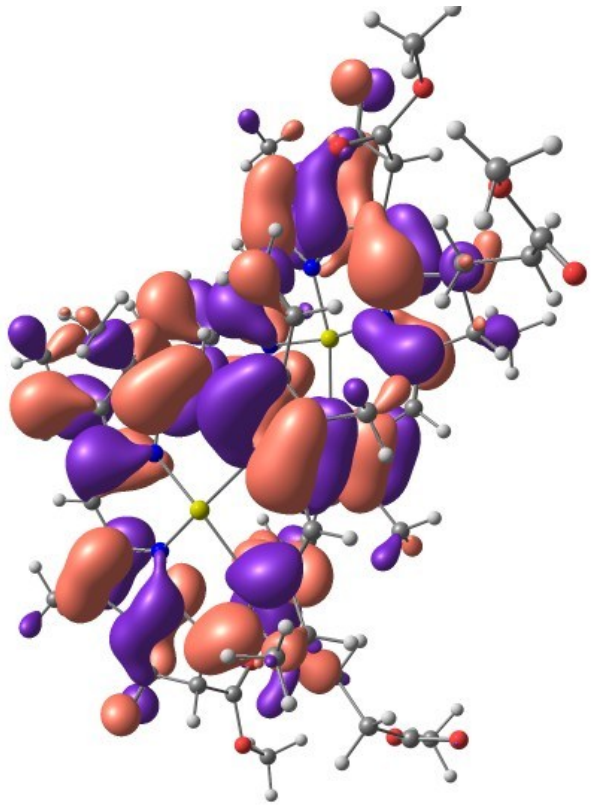

Figure 4S. Electron charge density distribution in the singly occupied molecular orbital of the primary donor cation, P_{800}^{+}, of the heliobacterial RC that is comprised of a BChl g_F' homodimer. The computational model is derived from the recent high-resolution X-ray crystal structure of the heliobacterial RC.[3]

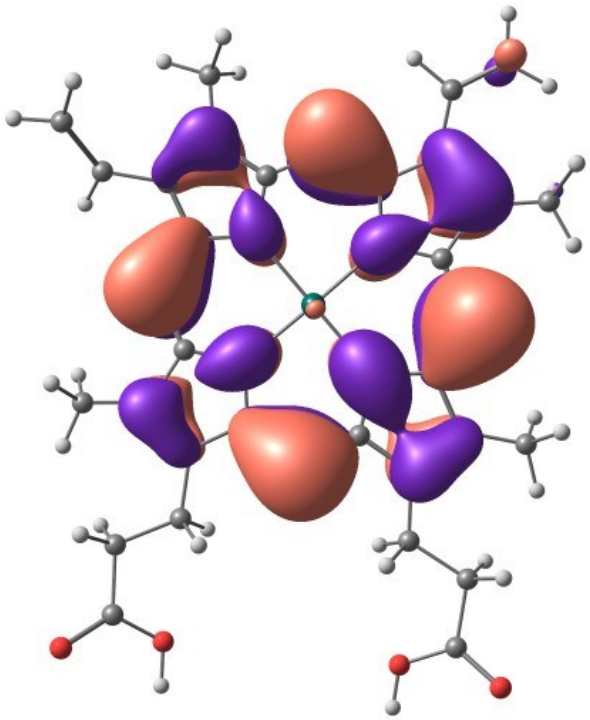

Table 1S. Experimental ^{67}Zn hyperfine (A) and quadrupolar (K) couplings for the Zn^{2+}-protoporphyrin IX cation that were obtained from experimental 2D HYSCORE measurements.

Nucleus	A_x (MHz)	A_y (MHz)	A_z (MHz)	A_{iso} (MHz)	K (MHz)	η
Zn^{I}	0.77 ± 0.05	0.84 ± 0.03	0.88 ± 0.03	0.83 ± 0.04	0.80 ± 0.03	0.23 ± 0.10

Table 2S. ^{67}Zn hyperfine (A) and quadrupolar (K) couplings for the Zn^{2+}-protoporphyrin cation that are obtained from DFT calculations.

Nucleus	A_x (MHz)	A_y (MHz)	A_z (MHz)	A_{iso} (MHz)	K (MHz)	η
Zn^{I}	0.77	0.84	0.88	0.83	1.28	0.06

Table 3S. ^{67}Zn hyperfine (A) and quadrupolar (K) parameters of the oxidized dimeric Zn^{2+}-BChl g_F′ cation that are obtained from DFT calculations.

Nucleus	A_x (MHz)	A_y (MHz)	A_z (MHz)	A_{iso} (MHz)	K (MHz)	η
Zn^{I}	0.52	0.64	0.71	0.62	1.35	0.14
Zn^{II}	0.49	0.61	0.68	0.59	1.35	0.14