

## Supporting Information

# Spin Alignment of Orthogonal $\pi$ -Radicals of Directly *meso*-Linked Porphyrin Arrays

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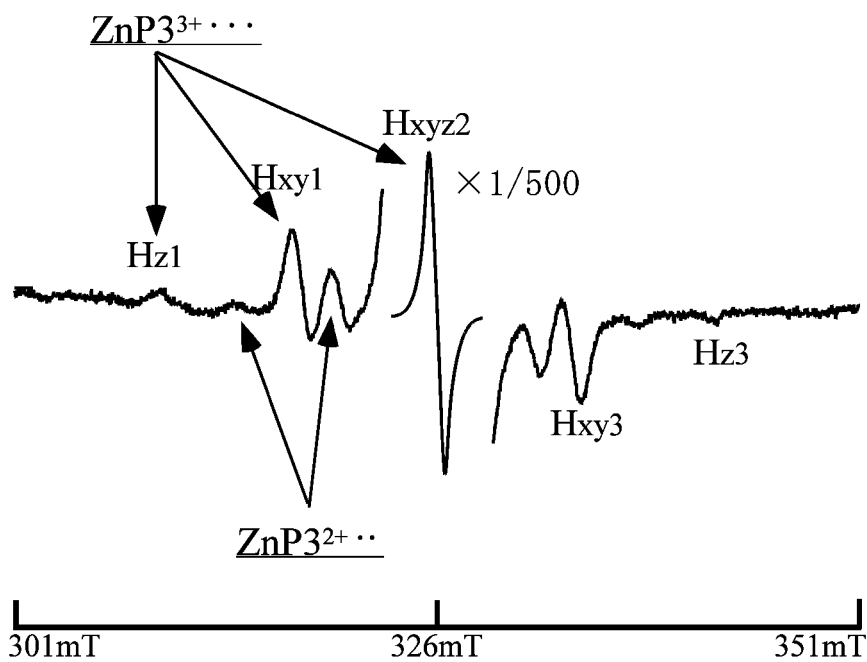
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**ZnP1** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 9.005 (s, 8H, 2, 3, 7, 8, 12, 13, 17, 18-*H*), 8.098 (d, J=1.5Hz, 8H, 5, 10, 15, 20-phenyl-*o*-H), 7.782 (t, J=3.1Hz, 4H, 5, 10, 15, 20-phenyl-*p*-H), 1.521 (s, 72H, 5, 10, 15, 20-phenyl-*tert*-butyl-H).

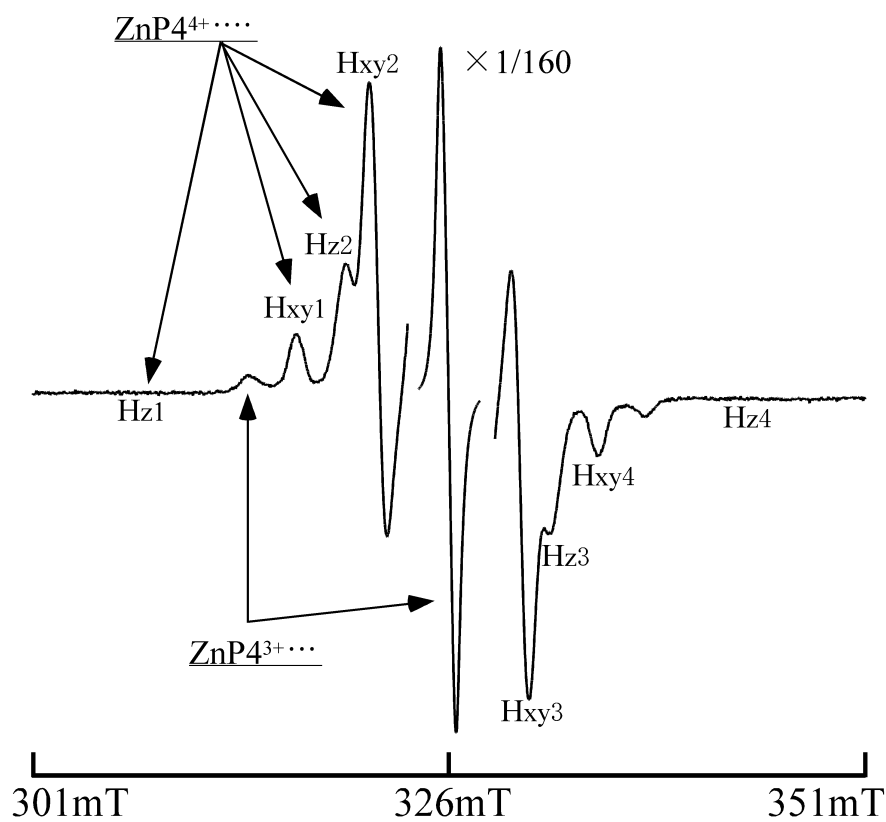
**ZnP2** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 9.057 (dd, J=4.50Hz, 8H, 12, 13, 17, 18, 12',13',17',18'-*H*), 8.708 (d, J=4.50Hz, 4H, 2, 8, 2', 8'-*H*), 8.170 (d, J=2.00Hz, 4H, 15, 15'-phenyl-*o*-H), 8.150 (d, J=4.50Hz, 4H, 3, 7, 3', 7'-*H*), 8.091 (d, J=2.00Hz, 8H, 10, 20, 10', 20'-phenyl-*o*-H), 7.827 (t, J=4.00Hz, 2H, 15, 15'-phenyl-*p*-H), 7.686 (t, J=3.50Hz, 4H, 10, 20, 10', 20'-phenyl-*p*-H), 1.568 (s, 36H, 15, 15' phenyl-*tert*-butyl-H), 1.434 (s, 72H, 10, 20, 10', 20'-phenyl-*tert*-butyl-H). UV-vis(CH<sub>2</sub>Cl<sub>2</sub>): max(nm)= 417, 458 (Soret band), 564, 607 (Q band).

**ZnP3**  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  9.075 (dd,  $J=4.50\text{Hz}$ , 8H, 12, 13, 17, 18, 12'', 13'', 17'', 18''- -H), 8.760 (dd,  $J=4.50\text{Hz}$ , 8H, 2, 8, 2'', 8'', 2', 8', 12', 18'- -H), 8.243 (dd,  $J=4.50\text{Hz}$ , 8H, 3, 7, 3'', 7'', 3', 7', 13', 17'- -H), 8.186 (d,  $J=1.83\text{Hz}$ , 4H, 15, 15''-phenyl-*o*-H), 8.123 (d,  $J=1.83\text{Hz}$ , 8H, 10, 20, 10'', 20''-phenyl-*o*-H), 8.080 (d,  $J=1.83\text{Hz}$ , 4H, 10', 20'-phenyl-*o*-H), 7.836 (t,  $J=3.36\text{Hz}$ , 2H, 15, 15''-phenyl-*p*-H), 7.715 (t,  $J=3.66\text{Hz}$ , 4H, 10, 20, 10'', 20''-phenyl-*p*-H), 7.584 (t,  $J=3.66\text{Hz}$ , 2H, 10', 20'-phenyl-*p*-H), 1.577 (s, 36H, 15, 15'' phenyl-*tert*-butyl-H), 1.464 (s, 72H, 10, 20, 10'', 20''-phenyl-*tert*-butyl-H), 1.342 (s, 36H, 10', 20' phenyl-*tert*-butyl-H). UV-vis( $\text{CH}_2\text{Cl}_2$ ): max(nm)=415.5, 476.5 (Soret band), 566.0 (Q band).

**ZnP4**  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  9.083 (dd,  $J=4.57\text{Hz}$ , 8H, 12, 13, 17, 18, 12''', 13''', 17''', 18'''- -H), 8.790 (ddd,  $J=4.57\text{Hz}$ , 12H, 2, 8, 2''', 8''', 2', 8', 2'', 8'', 12', 18', 12'', 18''- -H), 8.288 (ddd,  $J=4.57\text{Hz}$ , 12H, 3, 7, 3''', 7''', 3', 7', 3'', 7'', 13', 17', 13'', 17''- -H), 8.193 (d,  $J=1.83\text{Hz}$ , 4H, 15, 15'''-phenyl-*o*-H), 8.125 (dd,  $J=1.83\text{Hz}$ , 16H, 10, 20, 10''', 20''', 10', 20', 10'', 20''-phenyl-*o*-H), 7.814 (t,  $J=3.65\text{Hz}$ , 2H, 15, 15'''-phenyl-*p*-H), 7.723 (t,  $J=4.60\text{Hz}$ , 4H, 10, 20, 10''', 20'''-phenyl-*p*-H), 7.618 (t,  $J=3.40\text{Hz}$ , 4H, 10', 20', 10'', 20''-phenyl-*p*-H), 1.582 (s, 36H, 15, 15'''-phenyl-*tert*-butyl-H), 1.470 (s, 72H, 10, 20, 10''', 20'''-phenyl-*tert*-butyl-H), 1.373 (s, 72H, 10', 20', 10'', 20''-phenyl-*tert*-butyl-H). UV-vis( $\text{CH}_2\text{Cl}_2$ ): max(nm)=415.0, 485.0 (Soret band), 569.0 (Q band).



ESR Spectrum of **ZnP3<sup>3+...</sup>** at 170 K in CHCl<sub>3</sub> glass.



ESR Spectrum of **ZnP4<sup>4+...</sup>** at 170 K in CHCl<sub>3</sub> glass.