Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unexpected Diradical Character and Large Magnetic Spin Coupling in Modified Porphyrins Induced through Inverting Pyrrole Rings

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Supplementary Materials

Contents

1. All Calculated Data

(Including Total Energies of Relevant States, Deprotonation and Dehydrogenation Energies, Ionization Potentials, and Magnetic Spin Coupling Constants J, N-Methylation Effect, Meso-Tetraphenyl Substituent Effect)

Table S1. The Calculated Energies of the Closed-Shell Singlet ($\mathbf{E_{(CS)}}$/au), Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au) Ground States and Triplet ($\mathbf{E_{(T)}}$/au) at the B3LYP/6-311G (d,p) Level

Molecules	$E_{(CS)}$	$E_{(BS)}$	$(<S^2>)$	$E_{(T)}$	$(<S^2>)$
2H	-989.7867605	-989.7867605	(0.000)	-989.7298405	(2.059)
N-2H	-989.7479343	-989.7479343	(0.000)	-989.7154869	(2.074)
1NN-2H	-989.7016803	-989.7032246	(0.511)	-989.6964364	(2.116)
2NN-2H	-989.7019712	-989.7035074	(0.511)	-989.6966646	(2.115)
Mg	-1188.8402772	-1188.8402772	(0.000)	-1188.7762747	(2.045)
N-Mg	-1188.7581375	-1188.7581377	(0.000)	-1188.7244456	(2.052)
1NN-Mg	-1188.6659929	-1188.6667299	(0.390)	-1188.6605620	(2.099)
2NN-Mg	-1188.6661380	-1188.6668818	(0.395)	-1188.6609518	(2.098)
Zn	-2767.9919302	-2767.9919302	(0.000)	-2767.9272483	(2.045)
N-Zn	-2767.9275688	-2767.9275690	(0.000)	-2767.8924773	(2.057)
1NN-Zn	-2767.8581313	-2767.8585592	(0.300)	-2767.8499836	(2.102)
2NN-Zn	-2767.8585974	-2767.8589703	(0.283)	-2767.8502343	(2.100)

Table S2. The Single Point Calculated Energies of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au) Ground States and Triplet ($\mathbf{E_{(T)}}$/au) and the Corresponding Coupling Constants *J* (cm^{-1}) at the B3LYP/6-311G (d,p) Level. This Is to Examine only the NH/CH Exchange (Geometry Unrelaxed) Effect and the Exchange Modes Are Displayed in Figure S1.

Molecules	$E_{(BS)}$	$(<S^2>)$	$E_{(T)}$	$(<S^2>)$	J (cm^{-1})
1NN-2H	-989.6696329	(0.557)	-989.6659695	(2.117)	-551.31
2NN-2H	-989.6697295	(0.556)	-989.6644444	(2.124)	-739.66
1NN-Mg	-1188.6444999	(0.324)	-1188.6384367	(2.094)	-751.76
2NN-Mg	-1188.6445609	(0.322)	-1188.6387164	(2.094)	-724.01
1NN-Zn	-2767.8248267	(0.000)	-2767.8198226	(2.097)	-
2NN-Zn	-2767.8248267	(0.000)	-2767.8164308	(2.099)	-

Table S3. The Single Point Calculated Energies of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au, in fact a Closed-Shell State) Ground States and Triplet ($\mathbf{E_{(T)}}$/au) and the Corresponding Coupling Constants J (cm^{-1}) at the B3LYP/6-311G (d,p) Level. This Is Only to Examine the Deformation Effect and the Deformation Modes Are Displayed in Figure S2.

Molecules	$E_{(BS)}=E_{(CS)}$	$(<S^2>_{BS})$	$E_{(T)}$	$(<S^2>_{T})$	J (cm^{-1})
1NN-2H	-989.7513696	0.0	-989.6981437	2.059	-
2NN-2H	-989.7511626	0.0	-989.6981773	2.057	-
1NN-Mg	-1188.8182576	0.0	-1188.7543353	2.049	-
2NN-Mg	-1188.8181599	0.0	-1188.7545136	2.045	-
1NN-Zn	-2767.9621559	0.0	-2767.8985145	2.050	-
2NN-Zn	-2767.9619093	0.0	-2767.8986995	2.047	-

Table S4. The Calculated Energies of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au) Ground States and Triplet ($\mathbf{E_{(T)}}$/au) and the Corresponding Coupling Constants J (cm^{-1}) for All Dipyrrole-Inverted Porphine/Porphyrin and Their Doubly-Deprotonated and Doubly-Dehydrogenated Ones at the B3LYP/6-311G (d,p) Level.

Molecules	$E_{(BS)}$ $(<S^2>)$	$E_{(T)}$ $(<S^2>)$	J (cm^{-1})
1NN-2H	-989.7032246 (0.511)	-989.6964364 (2.116)	-928.2
$(1NN\text{-}2H)^{2-}$-$2H^{+}$	-988.5260484 (0.0)	-988.4919870 (2.072)	-
(1NN-2H)-2H	-988.4473880 (0.0)	-988.4351435 (2.046)	-
2NN-2H	-989.7035074 (0.511)	-989.6966646 (2.115)	-936.3
$(2NN\text{-}2H)^{2-}$-$2H^{+}$	-988.5259094 (0.0)	-988.4927354 (2.071)	-
(2NN-2H)-2H	-988.4508088 (0.0)	-988.4325330 (2.007)	-
1NN-Mg	-1188.6667299 (0.390)	-1188.6605620 (2.099)	-796.3
$(1NN\text{-}Mg)^{2-}$-$2H^{+}$	-1187.4807264 (0.0)	-1187.4460059 (2.058)	-
(1NN-Mg)-2H	-1187.4083915 (0.0)	-1187.3942922 (2.053)	-
2NN-Mg	-1188.6668818 (0.395)	-1188.6609518 (2.098)	-764.2
$(2NN\text{-}Mg)^{2-}$-$2H^{+}$	-1187.4803952 (0.0)	-1187.4478763 (2.063)	-
(2NN-Mg)-2H	-1187.4111067 (0.0)	-1187.3906201 (2.006)	-
1NN-Zn	-2767.8585592 (0.300)	-2767.8499836 (2.102)	-1044.5
$(1NN\text{-}Zn)^{2-}$ -$2H^{+}$	-2766.6746091 (0.0)	-2766.6376523 (2.059)	-
(1NN-Zn)-2H	-2766.6015066 (0.0)	-2766.5873631 (2.051)	-
2NN-Zn	-2767.8589703 (0.283)	-2767.8502343 (2.100)	-1055.2
$(2NN\text{-}Zn)^{2-}$-$2H^{+}$	-2766.6744441 (0.0)	-2766.6391572 (2.061)	-
(2NN-Zn)-2H	-2766.6045799 (0.0)	-2766.5840132 (2.007)	-

Table S5. The Calculated Energies of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au) Ground States and Triplet ($\mathbf{E_{(T)}}$/au) and the Corresponding Coupling Constants J (cm^{-1}) for All Dipyrrole-Inverted Meso-Tetraphenyl-Substituted Porphine/Porphyrin and Their Doubly-Deprotonated and Doubly-Dehydrogenated Ones at the B3LYP/6-311G (d,p) Level

Molecules	$\mathbf{E_{(BS)}}$ ($<S^2>$)	$\mathbf{E_{(T)}}$ ($<S^2>$)	$\boldsymbol{J}$ **(cm^{-1})**
(1NN-2H)(C_6H_5)$_4$	-1914.1293096 (0.476)	-1914.1246773 (2.100)	-625.8
(1NN-2H)(C_6H_5)$_4^{2-}$-2H$^+$	-1912.9708186 (0.0)	-1912.9257395 (2.049)	-
(1NN-2H)(C_6H_5)$_4$-2H	-1912.8718680 (0.0)	-1912.8546207 (2.042)	-
(2NN-2H)(C_6H_5)$_4$	-1914.1315934 (0.474)	-1914.1243511 (2.101)	-976.7
(2NN-2H)(C_6H_5)$_4^{2-}$-2H$^+$	-1912.9711119 (0.0)	-1912.9318841(2.045)	-
(2NN-2H)(C_6H_5)$_4$-2H	-1912.8754839 (0.0)	-1912.8507080 (2.006)	-
(1NN-Mg)(C_6H_5)$_4$	-2113.0925113 (0.324)	-2113.0855622 (2.089)	-864.7
(1NN-Mg)(C_6H_5)$_4^{2-}$-2H$^+$	-2111.9239939 (0.0)	-2111.8908288 (2.042)	-
(1NN-Mg)(C_6H_5)$_4$-2H	-2111.8317216 (0.0)	-2111.8114885 (2.048)	-
(2NN-Mg)(C_6H_5)$_4$	-2113.0941878 (0.309)	-2113.0872061 (2.085)	-862.6
(2NN-Mg)(C_6H_5)$_4^{2-}$-2H$^+$	-2111.9252482 (0.0)	-2111.8727366 (2.041)	-
(2NN-Mg)(C_6H_5)$_4$-2H	-2111.8371174 (0.0)	-2111. 809763 (2.007)	-
(1NN-Zn)(C_6H_5)$_4$	-3692.2854829 (0.263)	-3692.2796020 (2.085)	-708.2
(1NN-Zn)(C_6H_5)$_4^{2-}$-2H$^+$	-3691.1186755 (0.0)	-3691.0853875 (2.048)	-
(1NN-Zn)(C_6H_5)$_4$-2H	-3691.0263346 (0.0)	-3691.0045836(2.054)	-
(2NN-Zn)(C_6H_5)$_4$	-3692.2859198 (0.246)	-3692.2797979 (2.084)	-730.9
(2NN-Zn)(C_6H_5)$_4^{2-}$-2H$^+$	-3691.1186908 (0.0)	-3691.0873897 (2.048)	-
(2NN-Zn)(C_6H_5)$_4$-2H	-3691.0284356 (0.0)	-3691.0050067 (2.053)	-

Table S6. The Calculated Energies (in au) of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{(BS)}}$/au) Ground and Triplet ($\mathbf{E_{(T)}}$/au) States and the Coupling Constants J (cm^{-1}) for All Dipyrrole-Inverted N-Methylated Porphine/Porphyrins at the B3LYP/6-311G(d,p) Level

Molecules	$\mathbf{E_{(BS)}}$ ($<S^2>$)	$\mathbf{E_{(T)}}$ ($<S^2>$)	$\boldsymbol{J}$ **(cm^{-1})**
1NNCH$_3$-2H	-1068.3419276 (0.443)	-1068.3345313 (2.115)	-971.0
2NNCH$_3$-2H	-1068.3422379 (0.453)	-1068.3348564 (2.112)	-976.6
1NNCH$_3$-Mg	-1267.3054690 (0.319)	-1267.2986847 (2.097)	-837.5
2NNCH$_3$-Mg	-1267.3057057 (0.322)	-1267.2990313 (2.095)	-826.4
1NNCH$_3$-Zn	-2846.4972443 (0.211)	-2846.4879481 (2.099)	-1080.3
2NNCH$_3$-Zn	-2846.4977119 (0.197)	-2846.4882313 (2.097)	-1094.8

Table S7. The Calculated Energies of the Ground States (**E**/au) and N-hydrogen Single Hydrogen Dissociation Energies ($\Delta E_{(-H)}$/eV) or N-proton Single Proton Dissociation Energies ($\Delta E_{(-H+)}$/eV) for All Dipyrrole-Inverted Porphine/Porphyrins at the B3LYP/6-311G (d,p) Level

Molecules	**E**	$\Delta E_{(-H)}$	$\Delta E_{(-H+)}$
1NN-2H	-989.7032246 (BS)	3.23	14.58
(1NN-2H)-H	-989.0847545 (doublet)		
$(1NN\text{-}2H)^{-}$-H^{+}	-989.1672075 (CS)		
2NN-2H	-989.7035074 (BS)	3.22	14.58
(2NN-2H)-H	-989.0850475 (doublet)		
$(2NN\text{-}2H)^{-}$-H^{+}	-989.1674925 (CS)		
1NN-Mg	-1188.6667299 (BS)	3.30	14.69
(1NN-Mg)-H	-1188.0456731 (doublet)		
$(1NN\text{-}Mg)^{-}$-H^{+}	-1188.1265382 (CS)		
2NN-Mg	-1188.6668818 (BS)	3.29	14.70
(2NN-Mg)-H	-1188.0460726 (doublet)		
$(2NN\text{-}Mg)^{-}$-H^{+}	-1188.1265664 (CS)		
1NN-Zn	-2767.8585592 (BS)	3.31	14.67
(1NN-Zn)-H	-2767.2373177 (doublet)		
$(1NN\text{-}Zn)^{-}$-H^{+}	-2767.3196120 (CS)		
2NN-Zn	-2767.8589703 (BS)	3.30	14.67
(2NN-Zn)-H	-2767.2377778 (doublet)		
$(2NN\text{-}Zn)^{-}$-H^{+}	-2767.3198852 (CS)		

Table S8. The Calculated Energies of the Broken-Symmetry Open-Shell Singlet ($\mathbf{E_{BS}}$/au) Ground States and Energies ($\mathbf{\Delta E_{PT}}$/eV) of Proton Transfer to a H_2O as a Proton Acceptor (i.e. Solvent-Assisted Deprotonation) for All Dipyrrole-Inverted Porphine/Porphyrins at the B3LYP/6-311G (d,p) Level. The Transfer Process Is Defined as: For Example for the (1NN-2H)···OH_2 → ((1NN-2H)$_{(-H+)}^{-}$)···H^+OH_2 Process, ΔE_{PT}>0 means endothermic.

Molecules	$\mathbf{E_{(BS)}}$	$\mathbf{\Delta E_{PT}}$
(1NN-2H)···OH_2	-1066.1995238	1.69
((1NN-2H)$_{(-H+)}^{-}$)···H^+OH_2	-1066.1374559	
(2NN-2H)···OH_2	-1066.1995077	1.67
((2NN-2H)$_{(-H+)}^{-}$)···H^+OH_2	-1066.1383050	
(1NN-Mg)···OH_2	-1265.1605430	1.77
((1NN-Mg)$_{(-H+)}^{-}$)···H^+OH_2	-1265.0952500	
(2NN-Mg)···OH_2	-1265.1605559	1.78
((2NN-Mg)$_{(-H+)}^{-}$)···H^+OH_2	-1265.0952413	
(1NN-Zn)···OH_2	-2844.3538254	1.97
((1NN-Zn)$_{(-H+)}^{-}$)···H^+OH_2	-2844.2816143	
(2NN-Zn)···OH_2	-2844.3540425	1.93
((2NN-Zn)$_{(-H+)}^{-}$)···H^+OH_2	-2844.2832612	

Table S9. The Calculated Energies of the Ground States (**E**/au) and Single Electron or Dielectron Ionization Potentials (**IPs**/eV) at the B3LYP/6-311G (d,p) Level. For a Comparison, the Calculated and Experimental (in Parentheses) Values for Porphine (P-2H) Are Also Given.

Molecules	**E**	**IPa(-e)**	**IPa(-2e)**
P-2H	-989.7867605 (CS)	6.71 (6.9)	17.36
P-2H^{+}	-989.5403007 (doublet)		
P-2H^{2+}	-989.1487879 (CS)		
1NN-2H	-989.7032246 (BS)	5.60	15.37
(1NN-2H)$^{+}$	-989.4974550 (doublet)		
(1NN-2H)$^{2+}$	-989.1384846 (CS)		
2NN-2H	-989.7035074 (BS)	5.60	15.33
(2NN-2H)$^{+}$	-989.4977622 (doublet)		
(2NN-2H)$^{2+}$	-989.1400755 (CS)		
1NN-Mg	-1188.6667299 (BS)	5.48	15.01
(1NN-Mg)$^{+}$	-1188.4652007 (doublet)		
(1NN-Mg)$^{2+}$	-1188.1149330 (CS)		
2NN-Mg	-1188.6668818 (BS)	5.47	14.94
(2NN-Mg)$^{+}$	-1188.4656968 (doublet)		
(2NN-Mg)$^{2+}$	-1188.1176973 (CS)		
1NN-Zn	-2767.8585592 (BS)	5.55	15.16
(1NN-Zn)$^{+}$	-2767.6546029 (doublet)		
(1NN-Zn)$^{2+}$	-2767.3014929 (CS)		
2NN-Zn	-2767.8589703 (BS)	5.54	15.10
(2NN-Zn)$^{+}$	-2767.6552481 (doublet)		
(2NN-Zn)$^{2+}$	-2767.3039389 (CS)		

2. The Process Analyses of the CH/NH Exchange Effect

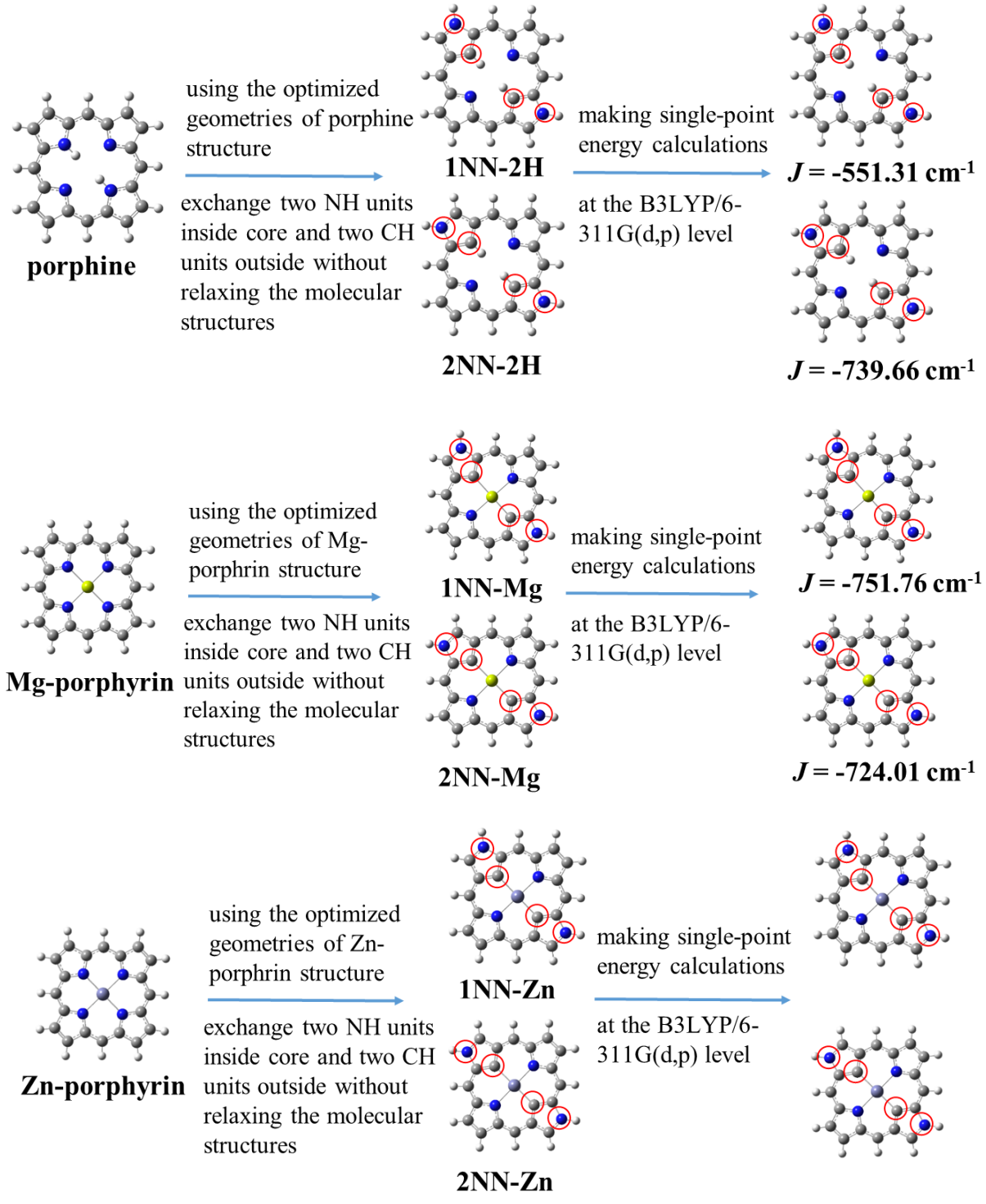


Figure S1. The process analyses of the CH/NH exchange effect for molecules (1NN-2H, 2NN-2H, 1NN-Mg, 2NN-Mg, 1NN-Zn and 2NN-Zn).

3. The Process Analyses of the Pure Geometric Deformation Effect

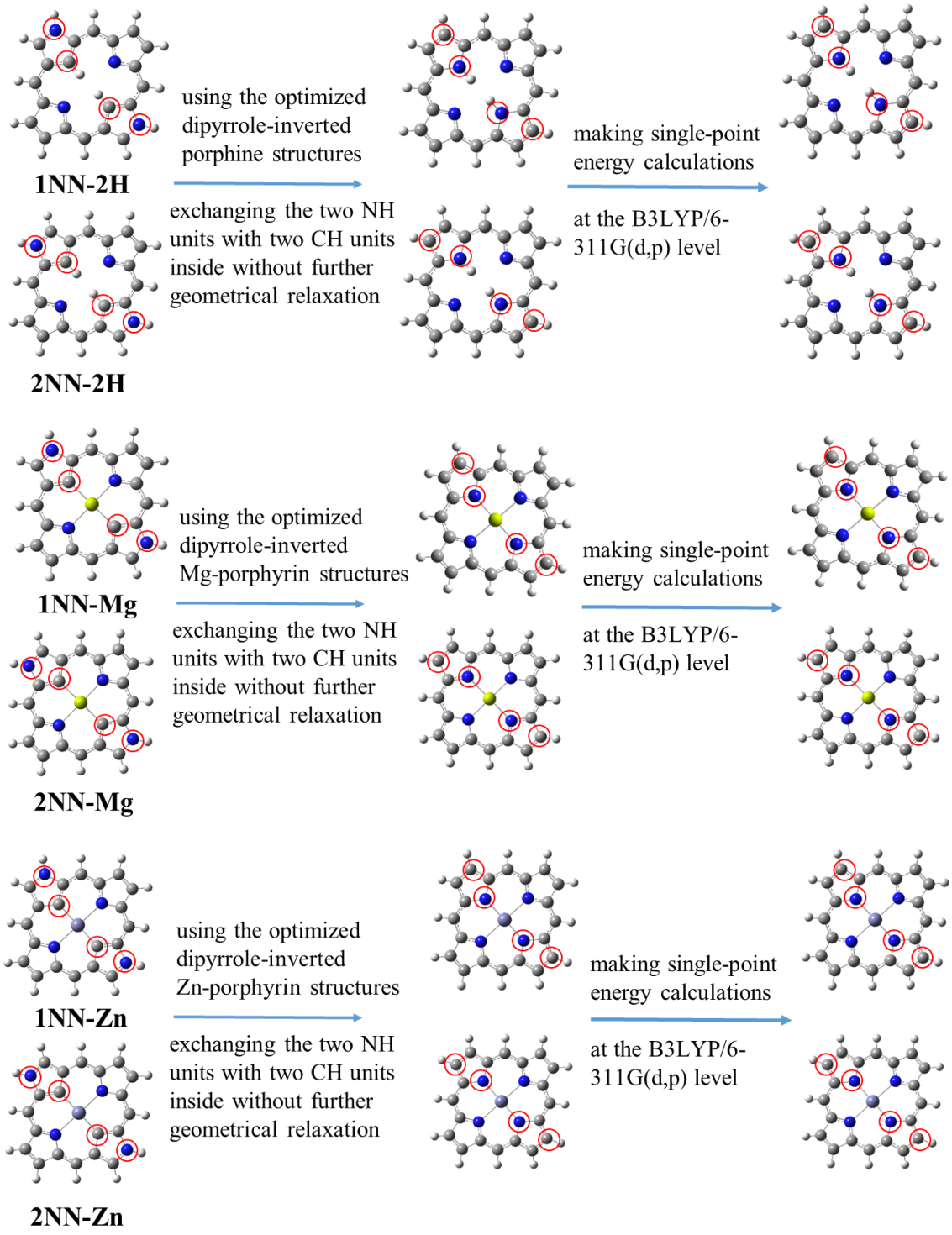


Figure S2. The process analyses of the pure geometric deformation effect for molecules (1NN-2H, 2NN-2H, 1NN-Mg, 2NN-Mg, 1NN-Zn and 2NN-Zn).

4. The Optimized Bond Lengths of the N-Zn, C-Zn, N-Mg and C-Mg Bonds

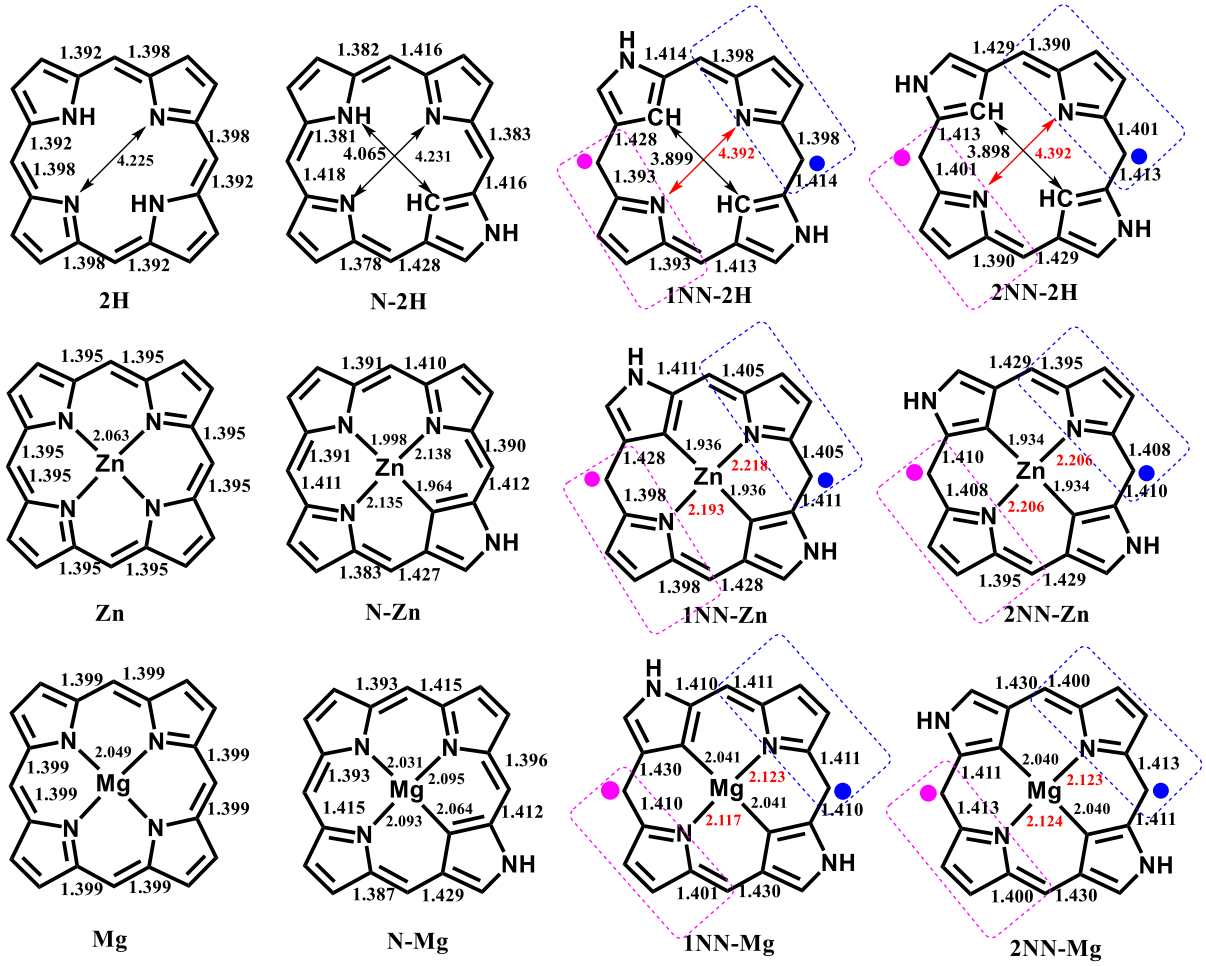


Figure S3. The optimized bond lengths for porphine, Mg/Zn-porphyrin, monopyrrole-inverted (N-2H, N-Zn and N-Mg) and dipyrrole-inverted porphyrin derivatives (1NN-2H, 2NN-2H, 1NN-Zn, 2NN-Zn, 1NN-Mg and 2NN-Mg).

5. The Spin Density Map and Spin Alternation Analysis

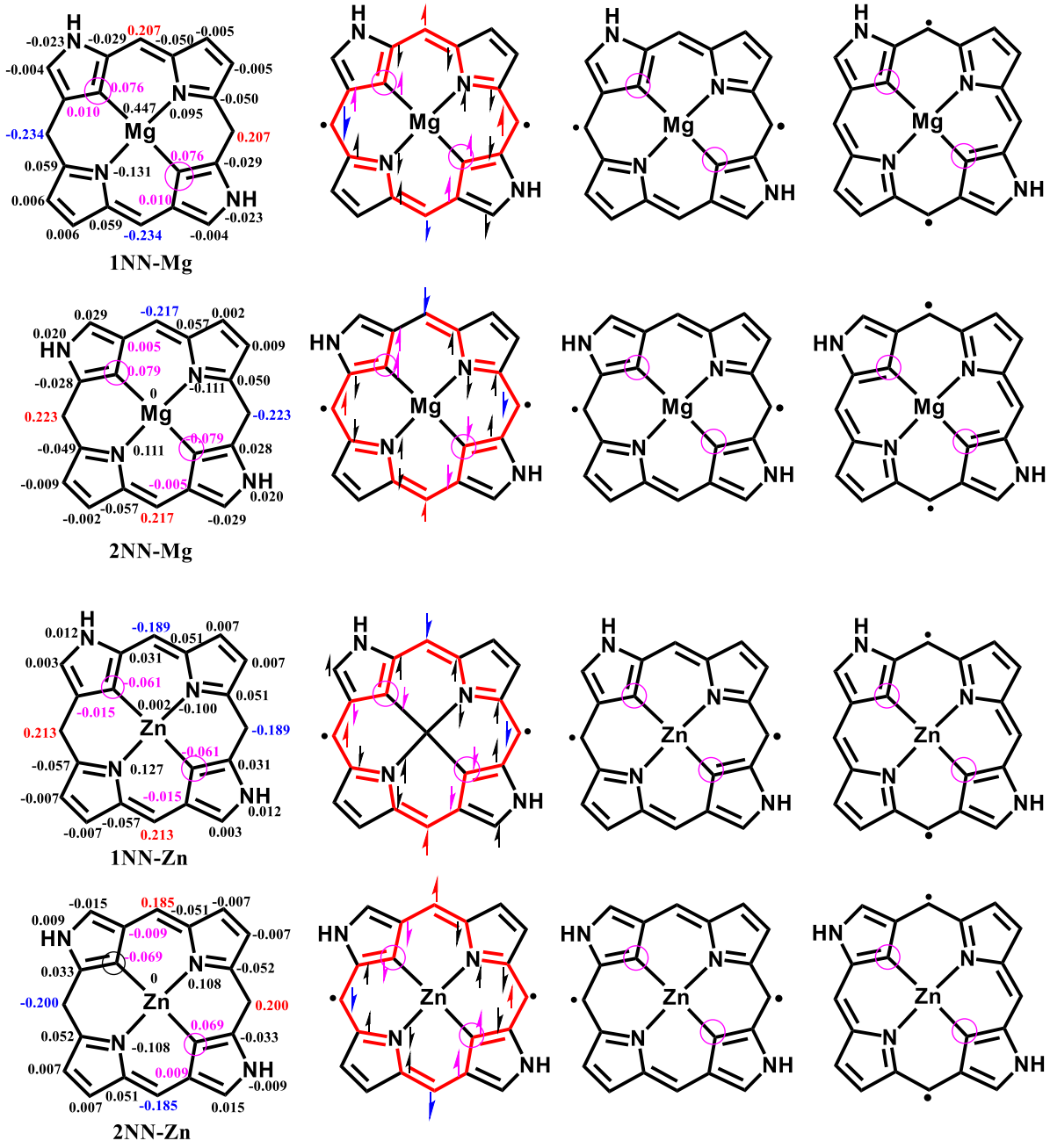


Figure S4. The spin density map and spin alternation analysis for the ground state dipyrrole-inverted Mg/Zn-porphyrin derivatives (1NN-Mg, 2NN-Mg, 1NN-Mg and 2NN-Mg). The inner π-conjugation circuits are indicated by the red-colored lines, and the pink-circled denote the =CH– unit and the pink number and arrow donate the same spin orientation of the =CH– unit and the adjacent one C atom.

6. The NICS(1) Values of All Porphyrin and Derivative

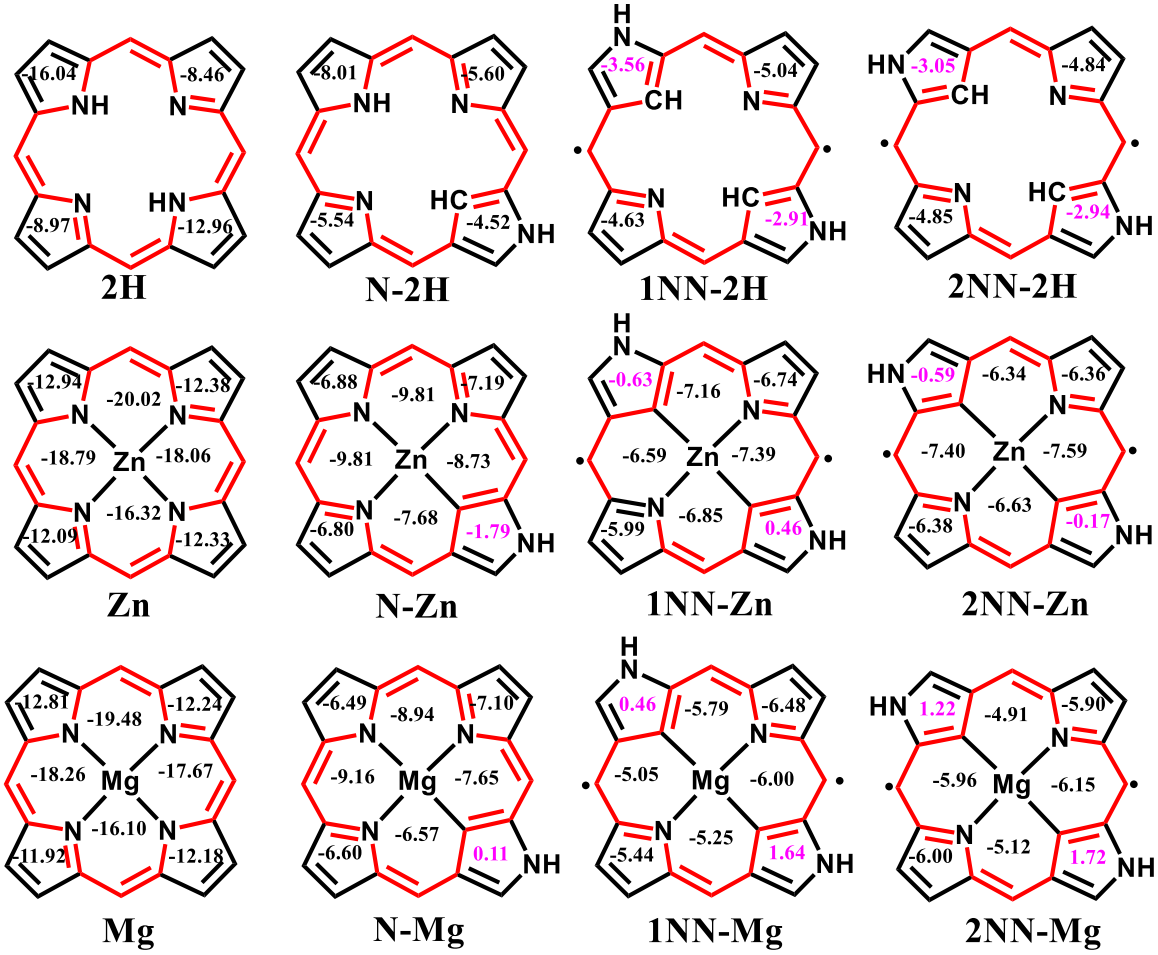
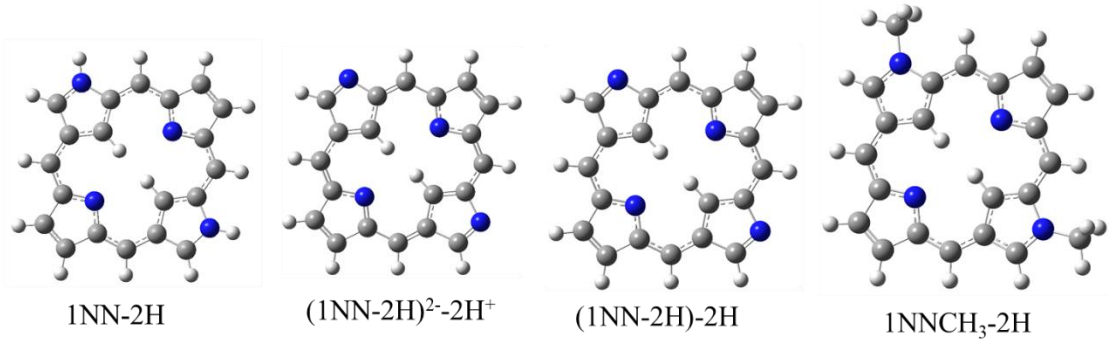
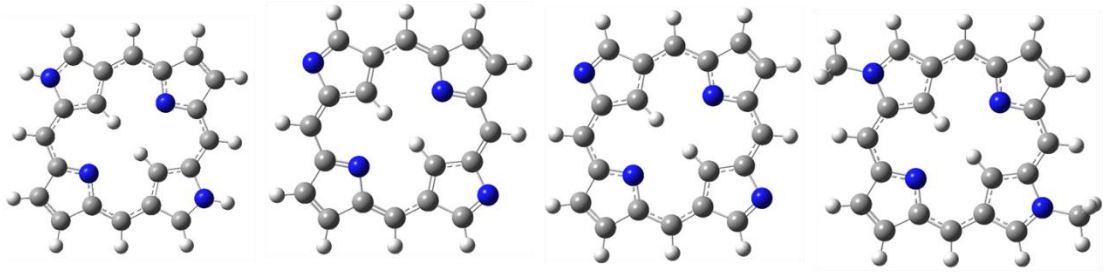


Figure S5. Calculated NICS (1) value (ppm) of each ring of all porphine and Mg/Zn-porphyrin and corresponding pyrrole-inverted porphine and Mg/Zn-porphyrin molecules. The inner π-conjugation circuits are indicated by the red-colored lines.

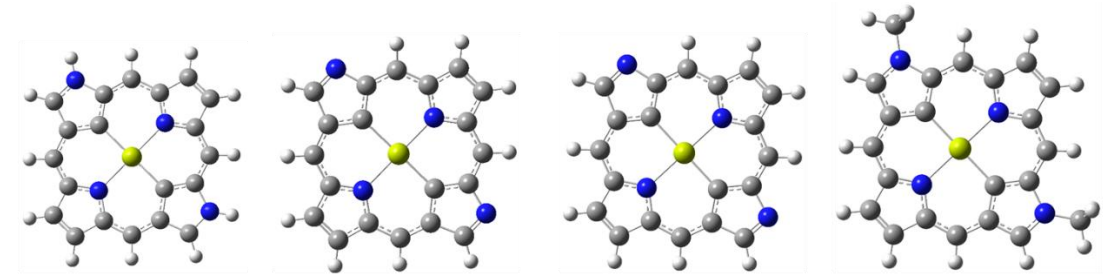
7. The Optimized Molecular Structures



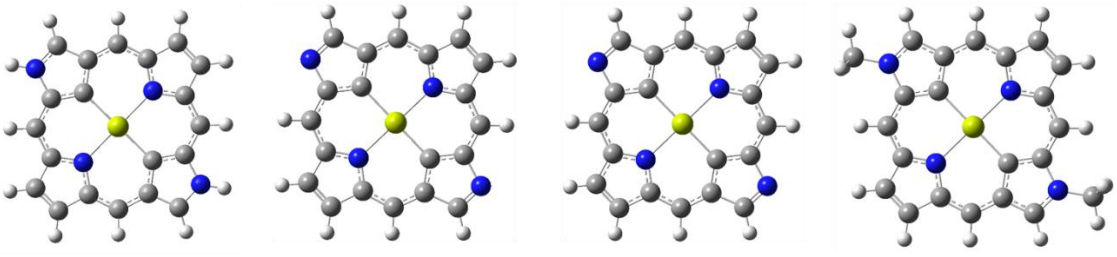
1NN-2H $(1NN\text{-}2H)^{2-}\text{-}2H^{+}$ (1NN-2H)-2H $1NNCH_3\text{-}2H$



2NN-2H $(2NN\text{-}2H)^{2-}\text{-}2H^{+}$ (2NN-2H)-2H $2NNCH_3\text{-}2H$



1NN-Mg $(1NN\text{-}Mg)^{2-}\text{-}2H^{+}$ (1NN-Mg)-2H $1NNCH_3\text{-}Mg$



2NN-Mg $(2NN\text{-}Mg)^{2-}\text{-}2H^{+}$ (2NN-Mg)-2H $2NNCH_3\text{-}Mg$

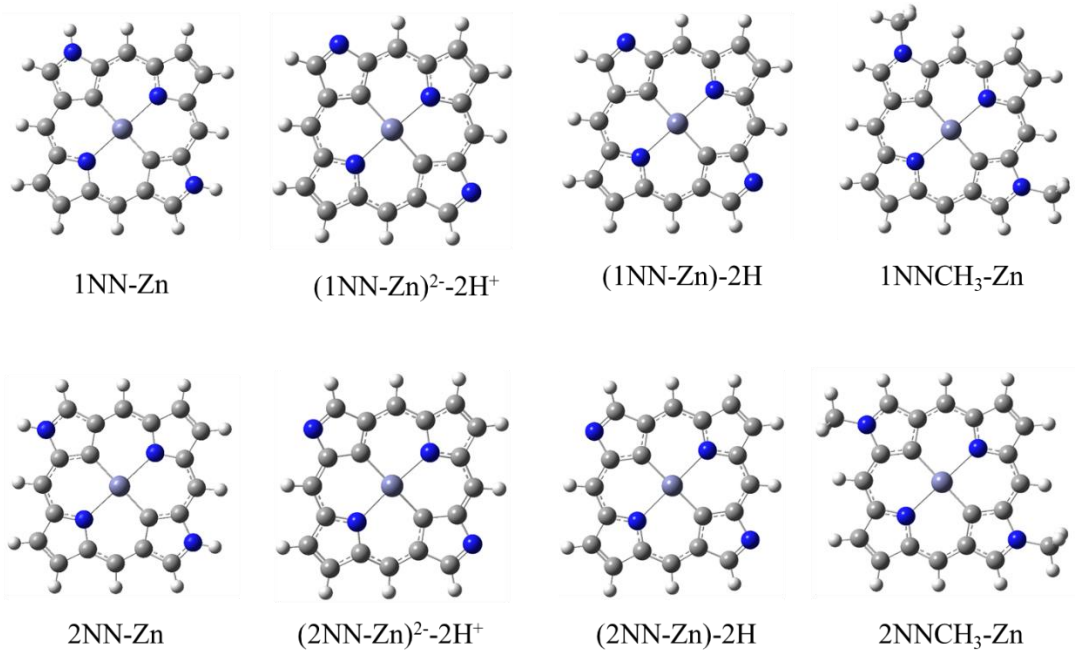
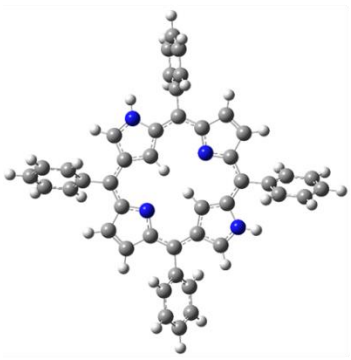
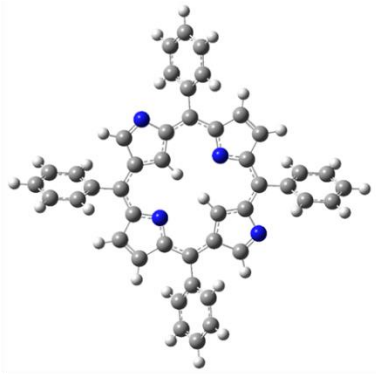


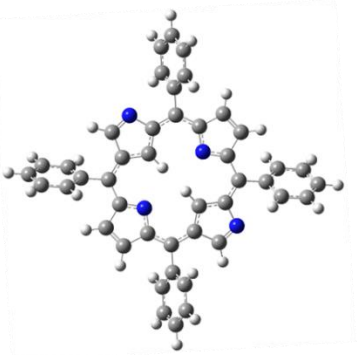
Figure S6. The optimized ground state molecular structures of dipyrrole-inverted porphine/porphyrin derivatives (1NN-2H, 2NN-2H, 1NN-Mg, 2NN-Mg, 1NN-Zn, and 2NN-Zn) and their corresponding doubly deprotonated structures ($(1NN\text{-}2H)^{2-}\text{-}2H^{+}$, $(2NN\text{-}2H)^{2-}\text{-}2H^{+}$, $(1NN\text{-}Mg)^{2-}\text{-}2H^{+}$, $(2NN\text{-}Mg)^{2-}\text{-}2H^{+}$, $(1NN\text{-}Zn)^{2-}\text{-}2H^{+}$ and $(2NN\text{-}Zn)^{2-}\text{-}2H^{+}$), doubly dehydrogenated structures ((1NN-2H)-2H, (2NN-2H)-2H , (1NN-Mg)-2H, (2NN-Mg)-2H, (1NN-Zn)-2H and (2NN-Zn)-2H), and N,N-methylated structures ($1NNCH_3$-2H, $2NNCH_3$-2H, $1NNCH_3$-Mg, $2NNCH_3$-Mg, $1NNCH_3$-Zn and $2NNCH_3$-Zn).



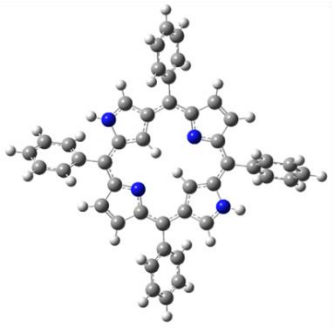
(1NN-2H)(C_6H_5)$_4$



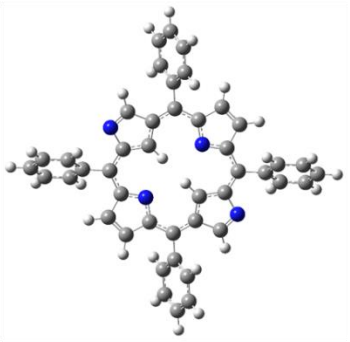
(1NN-2H)(C_6H_5)$_4^{2-}$-2H$^+$



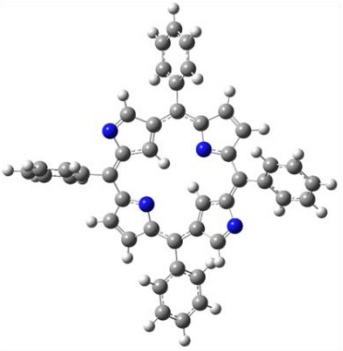
(1NN-2H)(C_6H_5)$_4$-2H



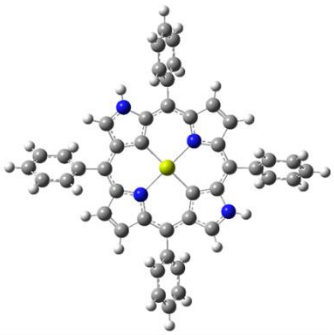
(2NN-2H)(C_6H_5)$_4$



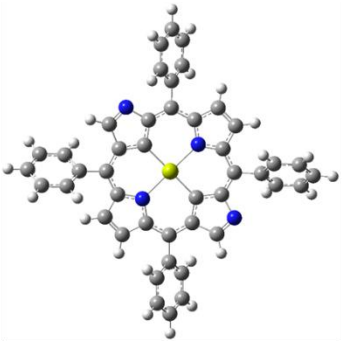
(2NN-2H)(C_6H_5)$_4^{2-}$-2H$^+$



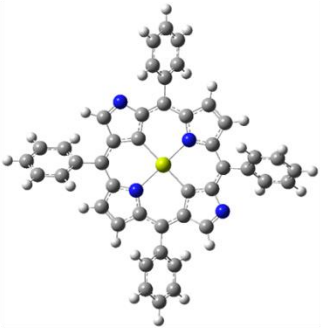
(2NN-2H)(C_6H_5)$_4$-2H



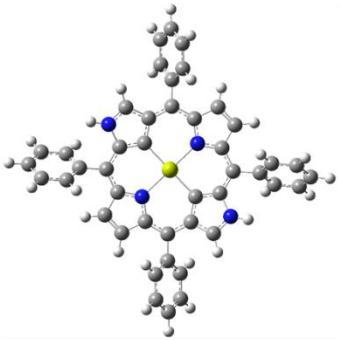
(1NN-Mg)(C_6H_5)$_4$



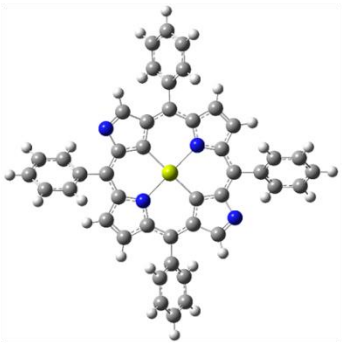
(1NN-Mg)(C_6H_5)$_4^{2-}$-2H$^+$



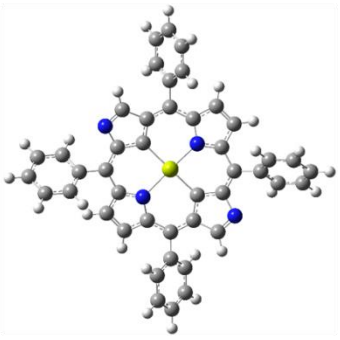
(1NN-Mg)(C_6H_5)$_4$-2H



(2NN-Mg)(C_6H_5)$_4$



(2NN-Mg)(C_6H_5)$_4^{2-}$-2H$^+$



(2NN-Mg)(C_6H_5)$_4$-2H

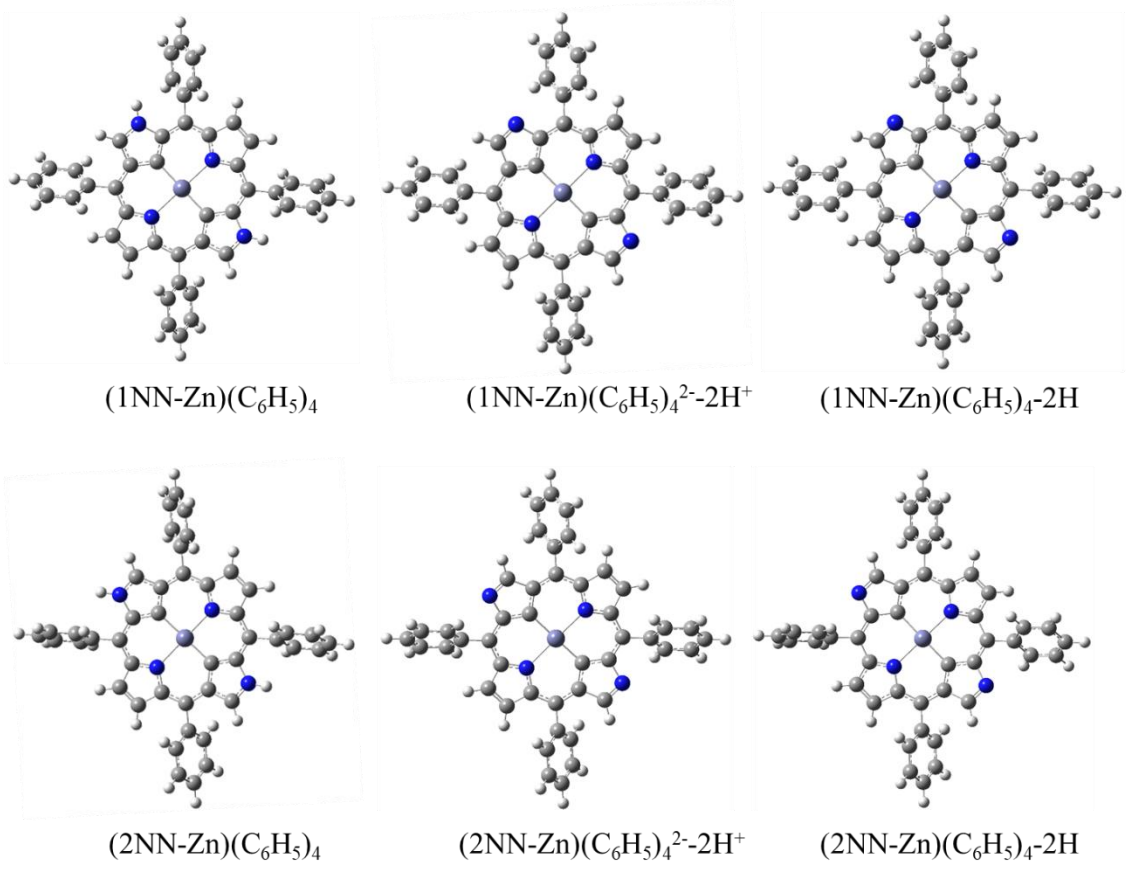


Figure S7. The optimized ground state molecular structures of dipyrrole-inverted Tetraphenyl porphyrin derivatives of porphine, Mg/Zn-porphyrin ((1NN-2H)$(C_6H_5)_4$, (2NN-2H)$(C_6H_5)_4$, (1NN-Mg)$(C_6H_5)_4$, (2NN-Mg)$(C_6H_5)_4$, (1NN-Zn)$(C_6H_5)_4$ and (2NN-Zn)$(C_6H_5)_4$) and their corresponding doubly deprotonated structures ((1NN-2H)$(C_6H_5)_4^{2-}$-$2H^+$, (2NN-2H)$(C_6H_5)_4^{2-}$-$2H^+$, (1NN-Mg)$(C_6H_5)_4^{2-}$-$2H^+$, (2NN-Mg)$(C_6H_5)_4^{2-}$-$2H^+$, (1NN-Zn)$(C_6H_5)_4^{2-}$-$2H^+$ and (2NN-Zn)$(C_6H_5)_4^{2-}$-$2H^+$) and doubly dehydrogenated structures ((1NN-2H)$(C_6H_5)_4$-2H, (2NN-2H)$(C_6H_5)_4$-2H, (1NN-Mg)$(C_6H_5)_4$-2H, (2NN-Mg)$(C_6H_5)_4$-2H, (1NN-Zn)$(C_6H_5)_4$-2H and (2NN-Zn)$(C_6H_5)_4$-2H).