Discriminate sensing of pyrophosphate using a new tripodal tetramine-based dinuclear Zn(II) complex under indicator displacement assay approach

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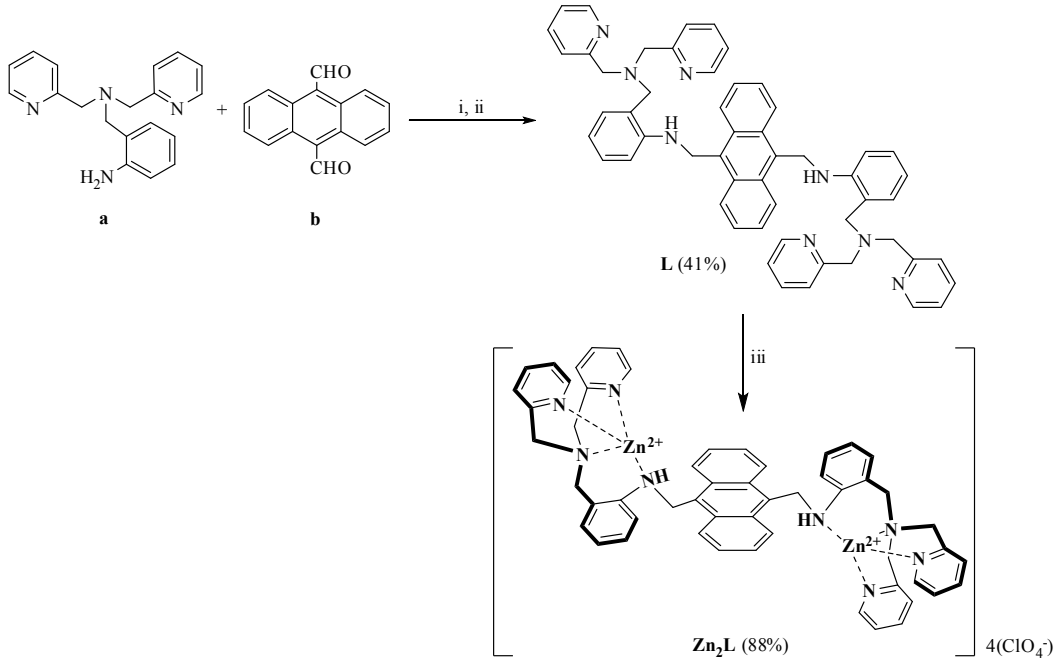
Content



Scheme S1. Synthetic procedure of **L** and **Zn_2L**. (i) acetronitrile, reflux 12 h, (ii) $NaBH_4$, MeOH, reflux 12 h, (iii) $Zn(ClO_4)_2$, EtOH, reflux 12 h.

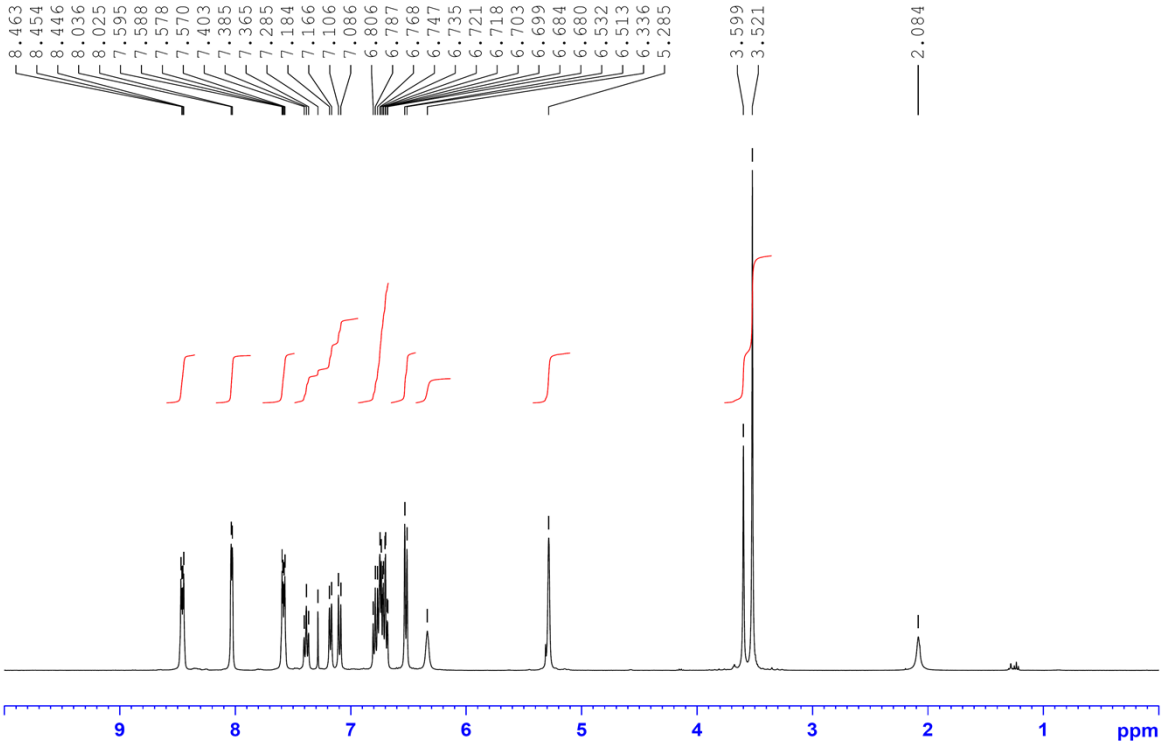


Figure S1.^{1}H-NMR spectrum of ligand **L** in $CDCl_3$.

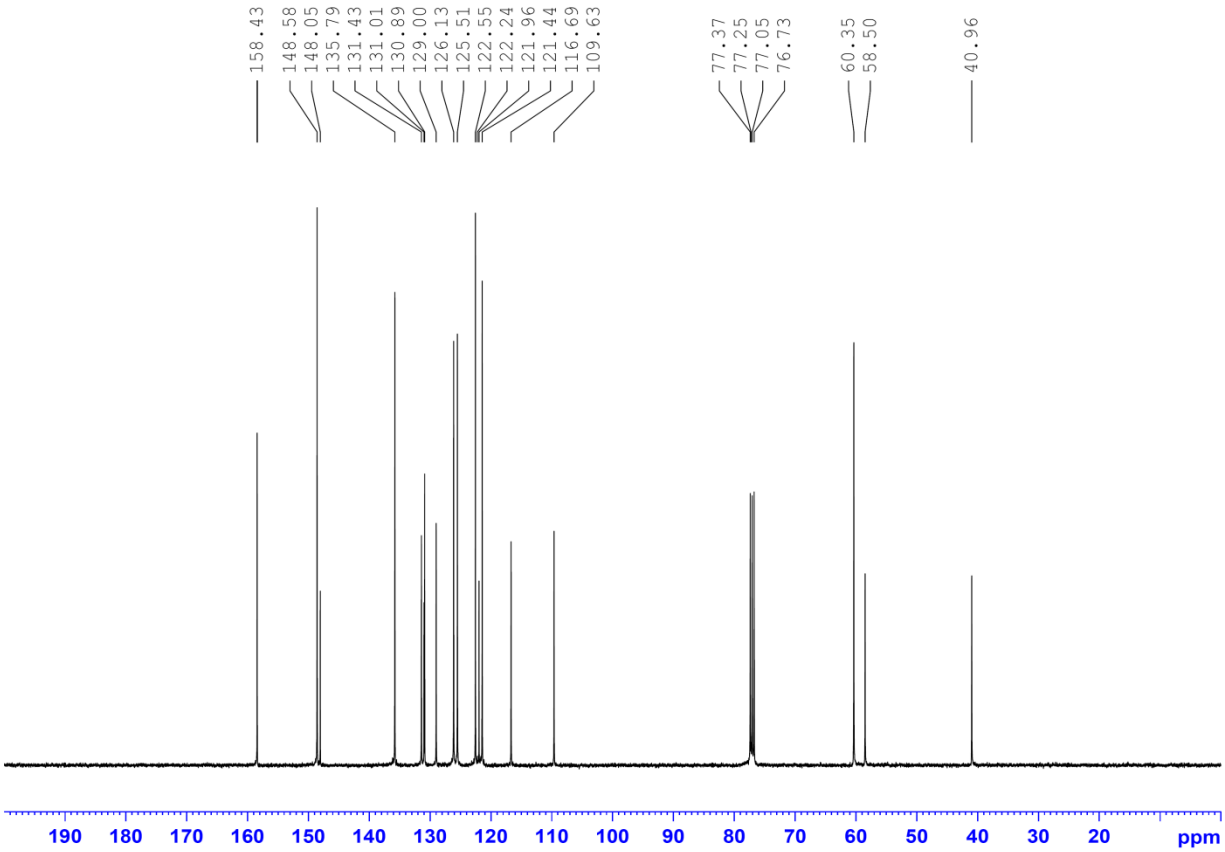


Figure S2. ^{13}C-NMR Spectrum of ligand **L** in $CDCl_3$.

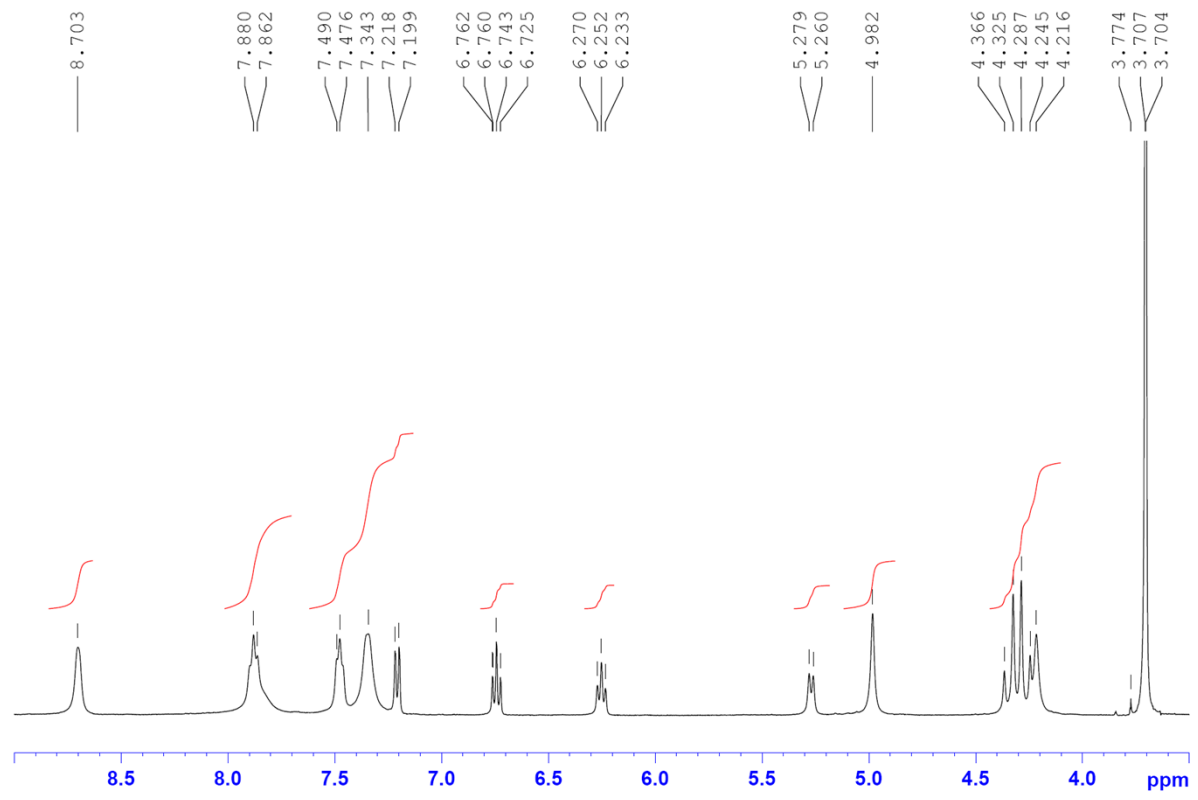


Figure S3. ^{1}H-NMR spectrum of **Zn_2L** in 20% (v/v) D_2O/CD_3CN.

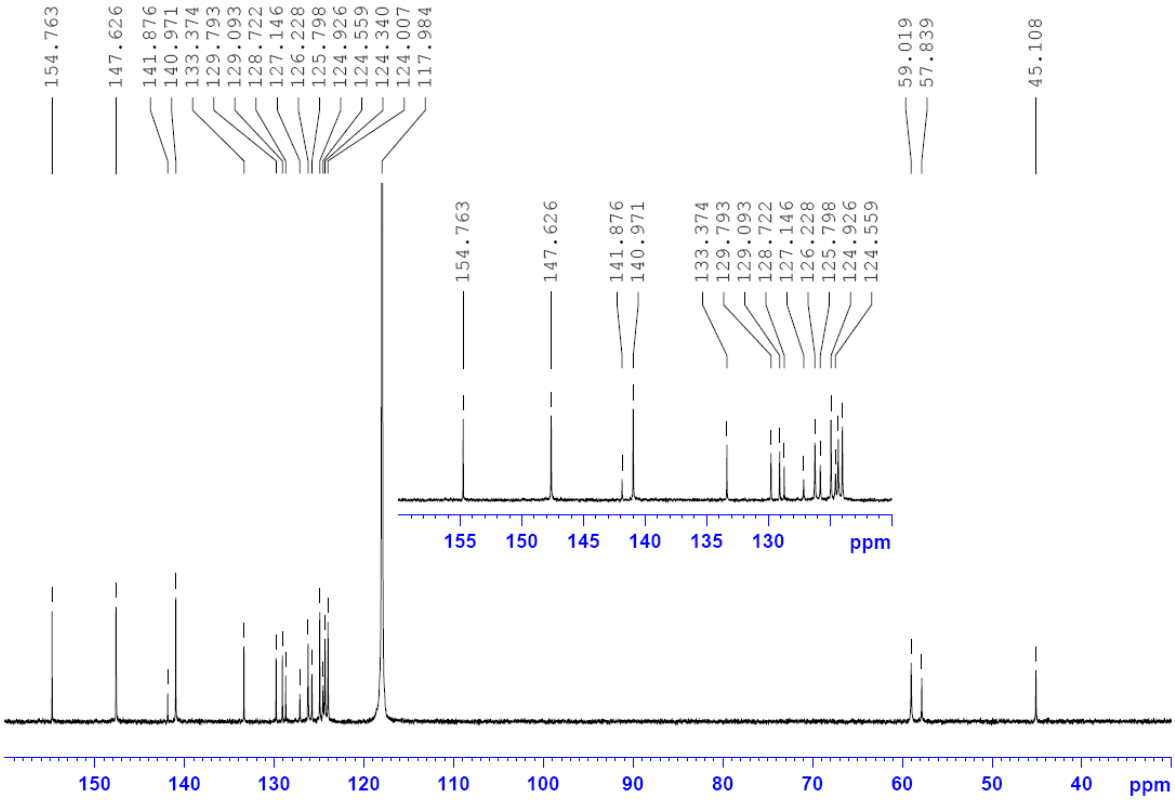


Figure S4. ^{13}C-NMR spectrum of **Zn_2L** in 20% (v/v) D_2O/CD_3CN.

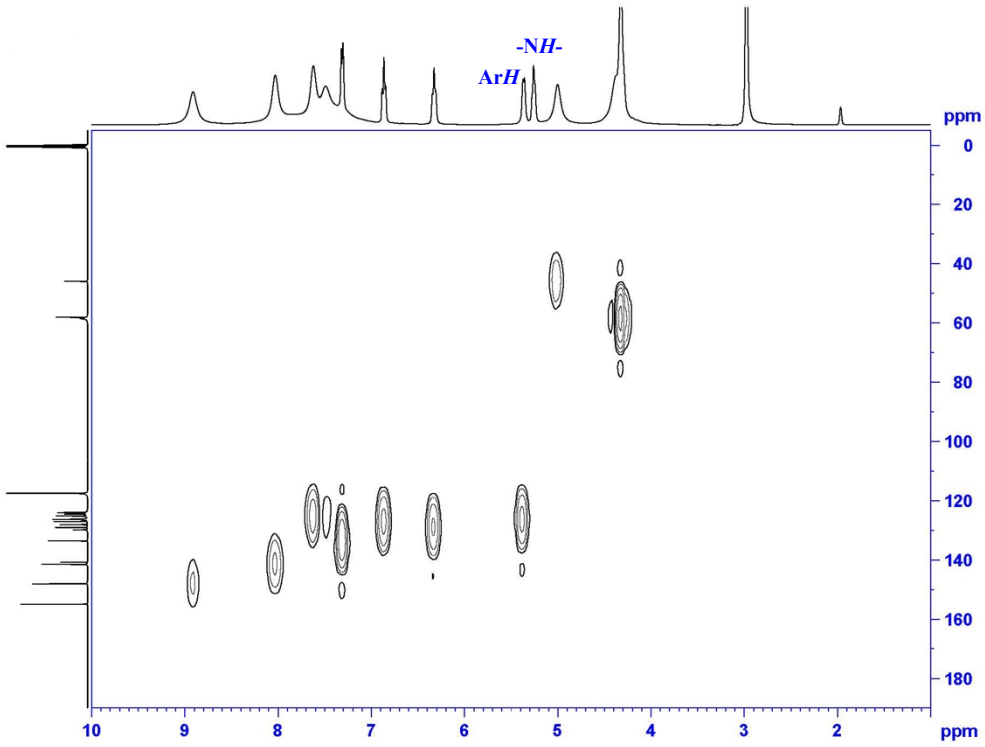


Figure S5. HMQC-NMR spectrum of **Zn_2L** in CD_3CN.

Table S1 Total and relative energies of all the B3LYP/LANL2DZ–optimized structures of six conformers of the dimeric 2:2 species.

Conformers [a]	E_{total} [b]	ΔE_{rel} [c]
C1	-6392.7827862	75.37
C2 [d]	-6392.9028947	0.00
C3	-6392.8176487	53.49
P1	-6392.7687205	84.20
P2	-6392.7596734	89.87
P3	-6392.7567471	91.71

[a] Conformers are named according to cross (C) or parallel (P) alignment of two anthracene units of the dimeric species. [b] Total energies are in au. [c] Relative energies compared with the most stable conformer (C2), in kcal/mol. [d] The most stable conformer.

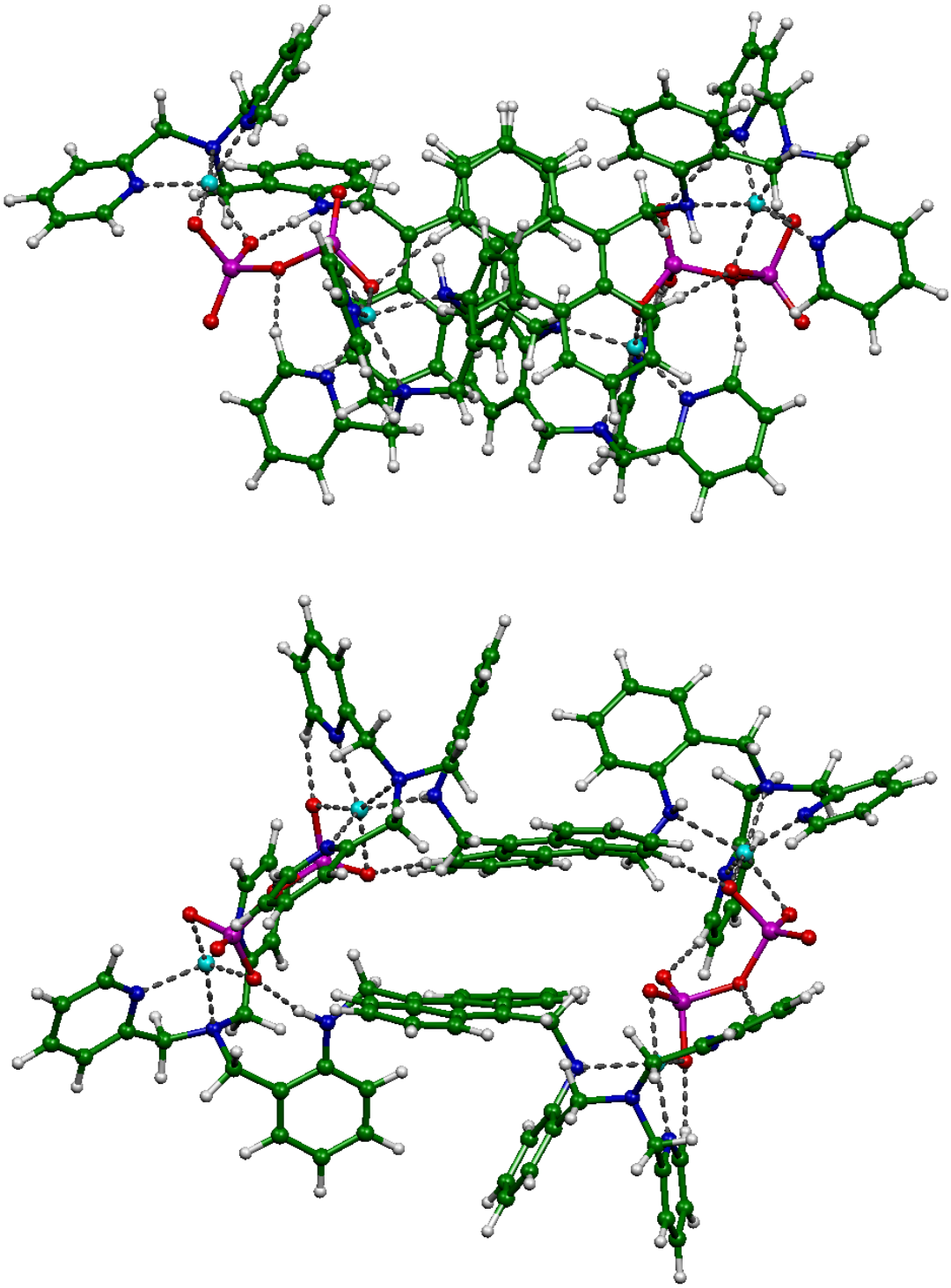


Figure S6. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of C1 conformer. Top and bottom images are top and front views, respectively.

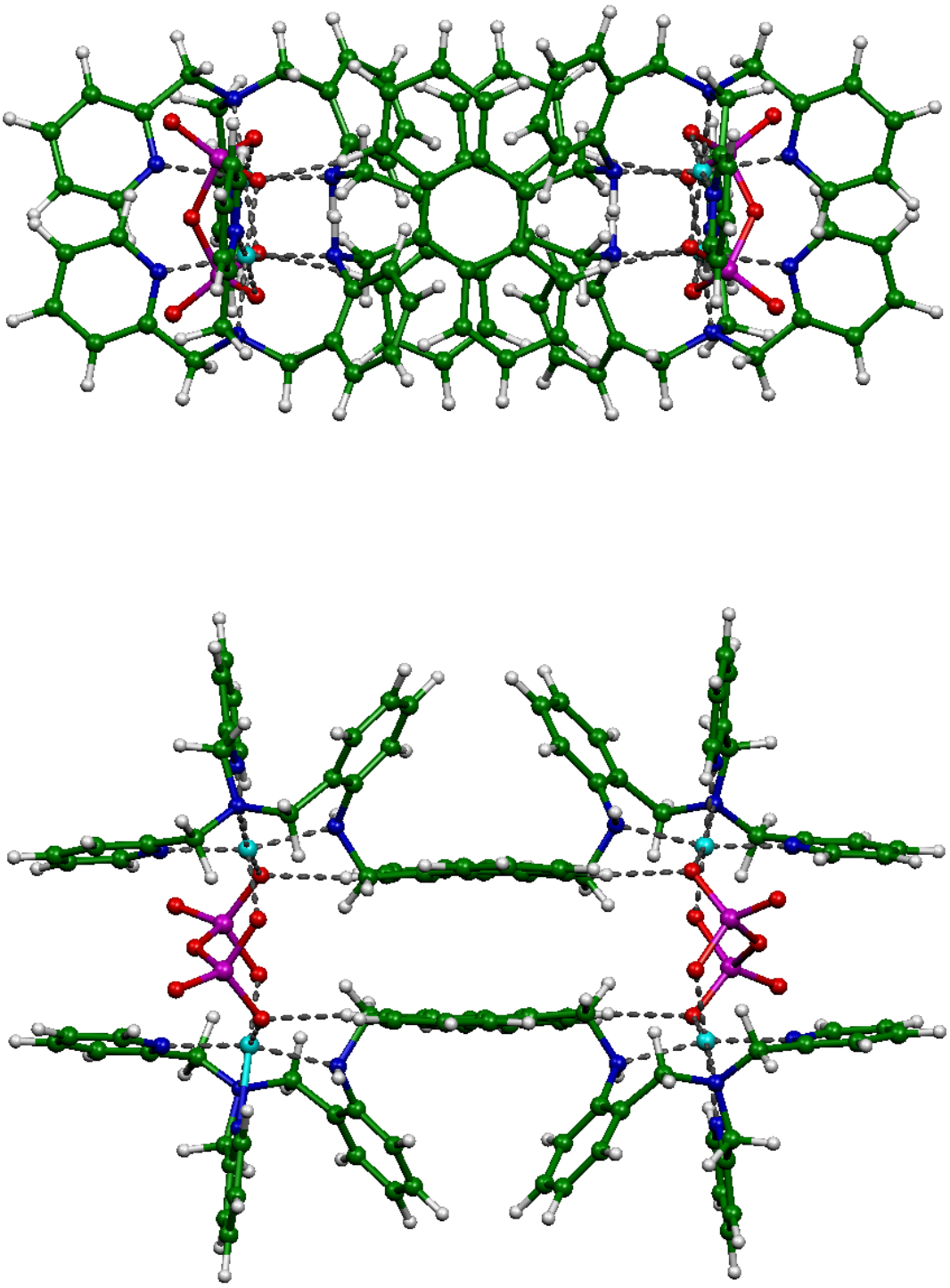


Figure S7. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of C2 conformer as the most stable one. Top and bottom images are top and front views, respectively.

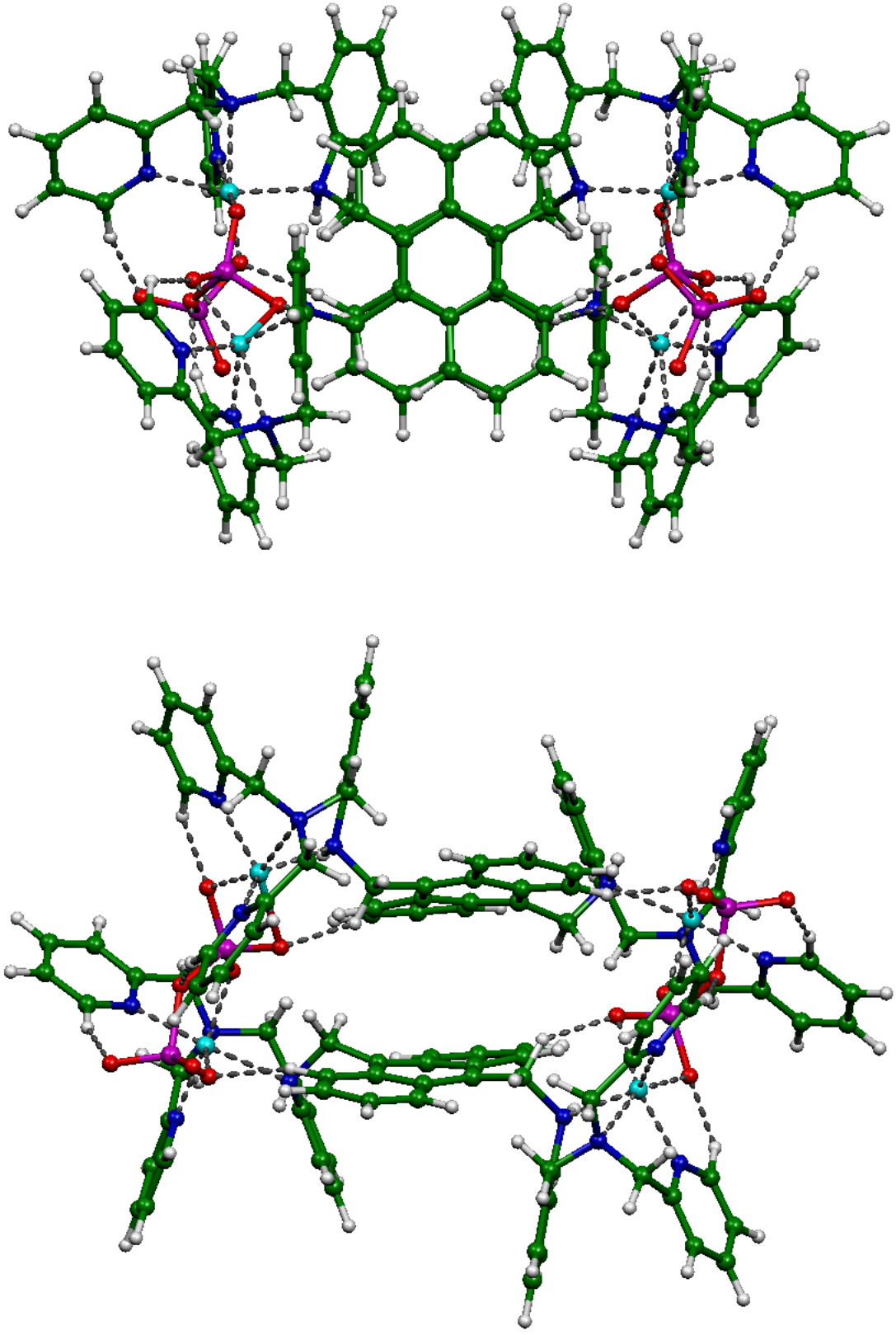


Figure S8. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of C3 conformer. Top and bottom images are top and front views, respectively.

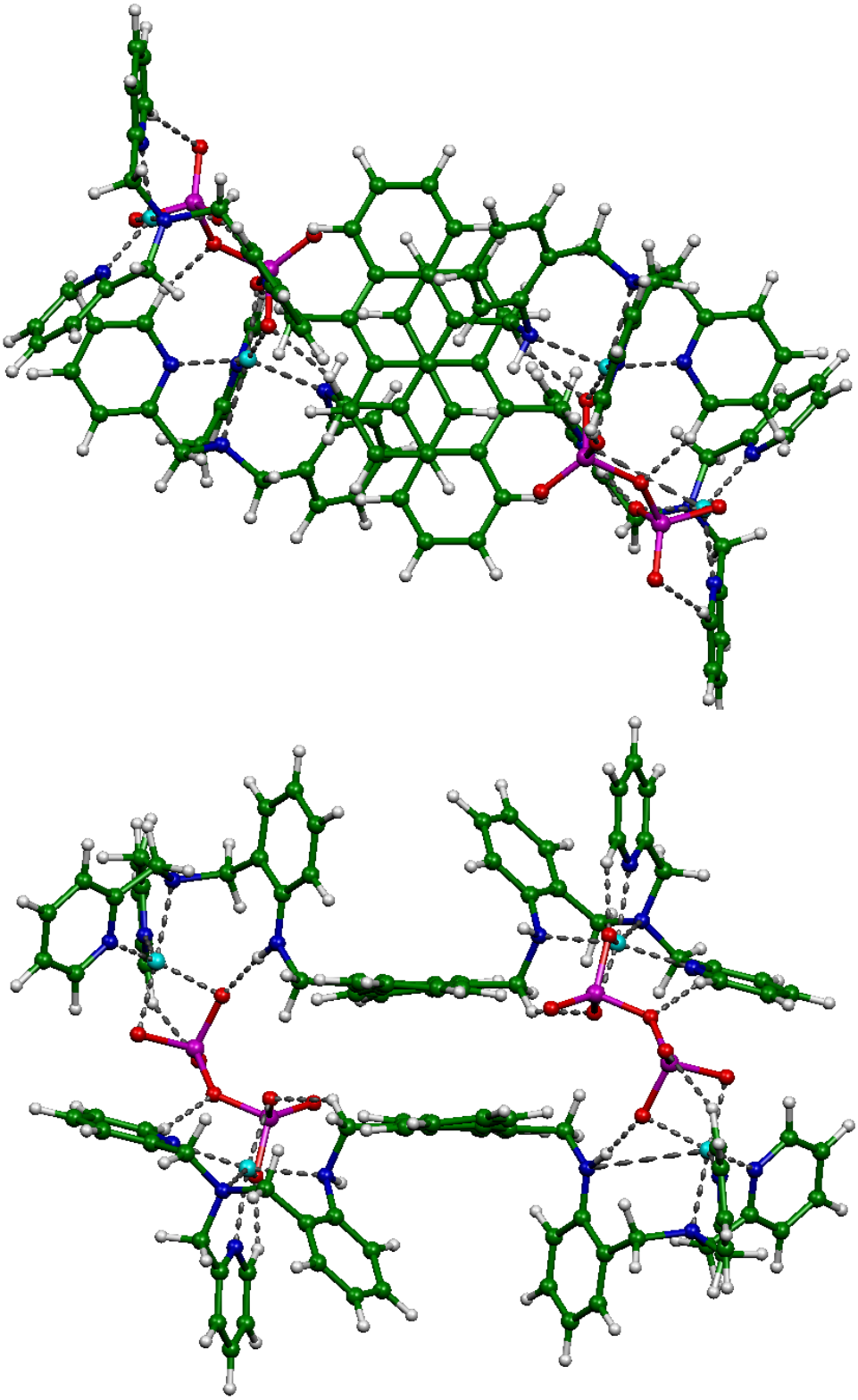


Figure S9. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of P1 conformer. Top and bottom images are top and front views, respectively.

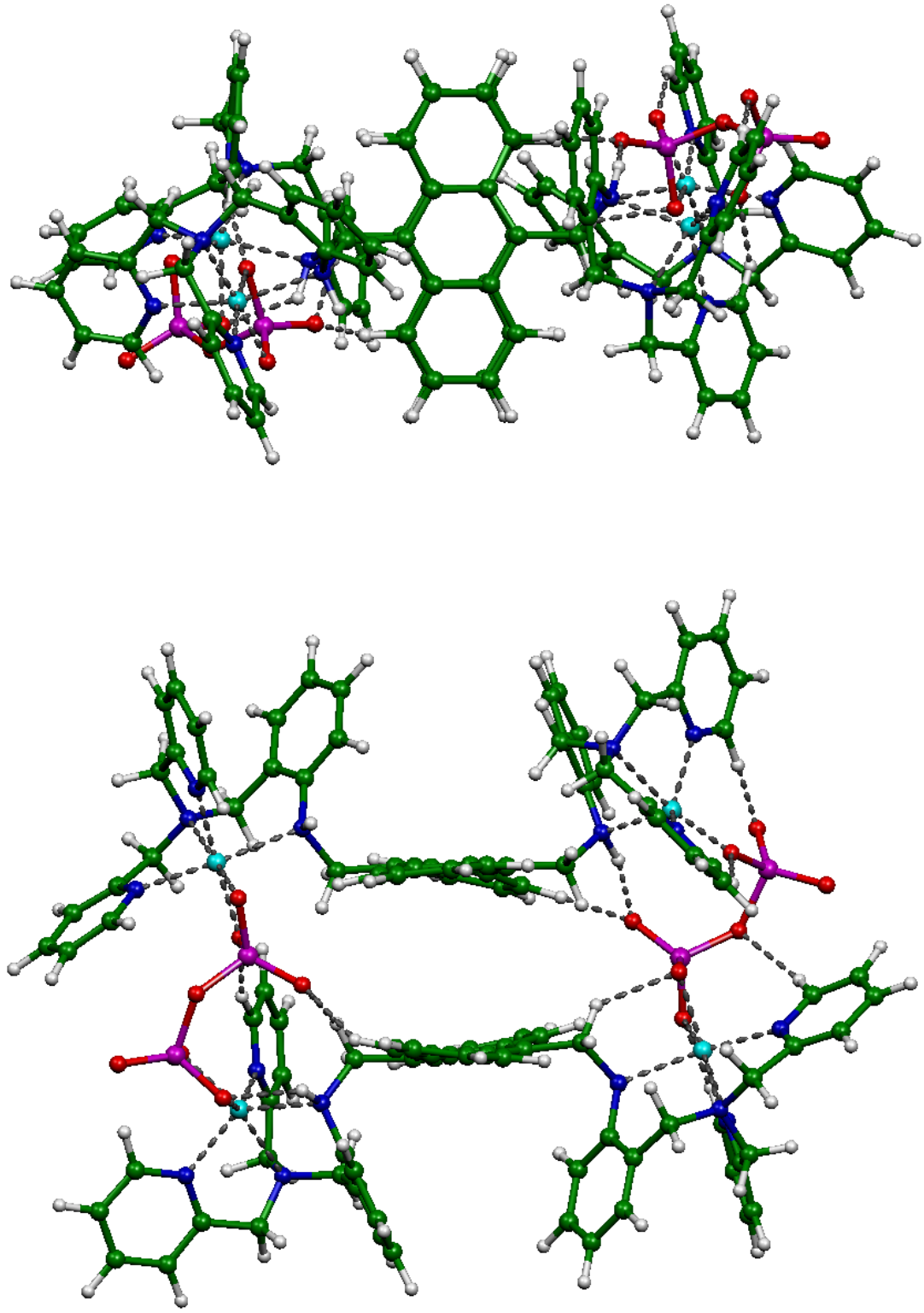


Figure S10. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of P2 conformer. Top and bottom images are top and front views, respectively.

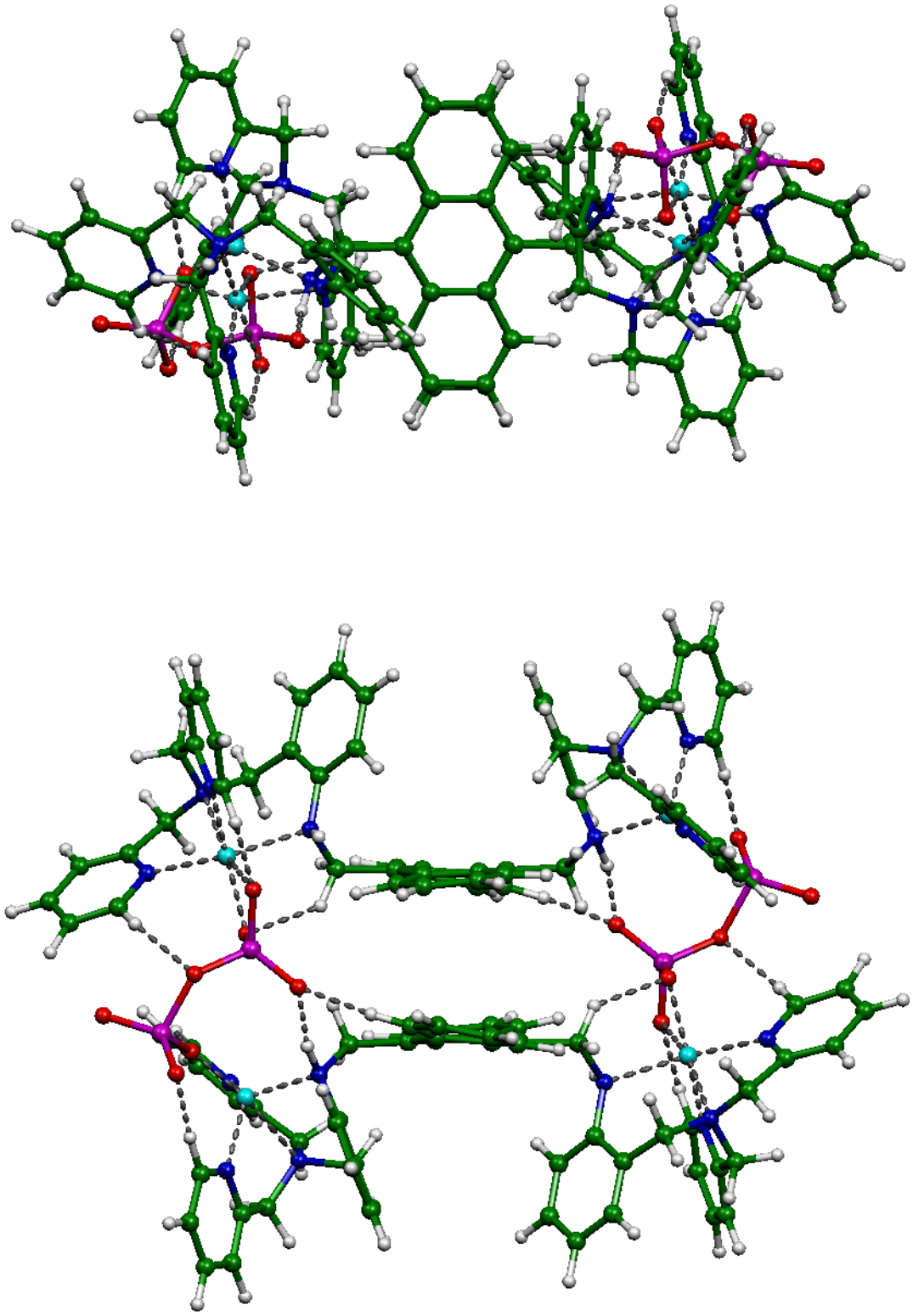


Figure S11. DFT/B3LYP/LANL2DZ-optimized structure of the dimeric 2:2 species of P3 conformer. Top and bottom images are top and front views, respectively.

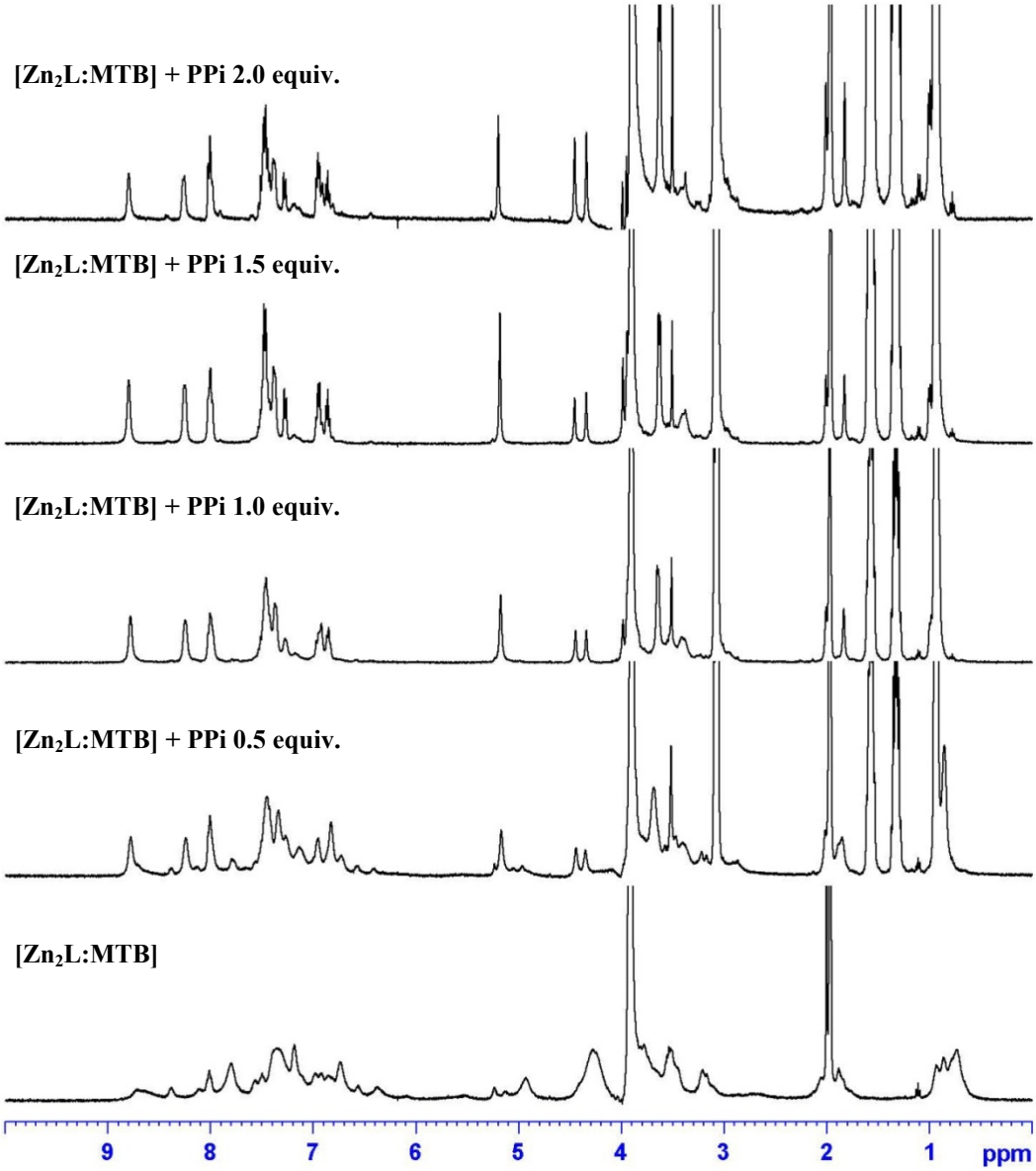


Figure S12. ^{1}H NMR spectra of 1:1 ratio of ensemble formation between **Zn_2L:MTB** (5 mM) upon addition of various concentrations of **PPi** (0.05 M) in 20% (v/v) D_2O:CD_3CN.

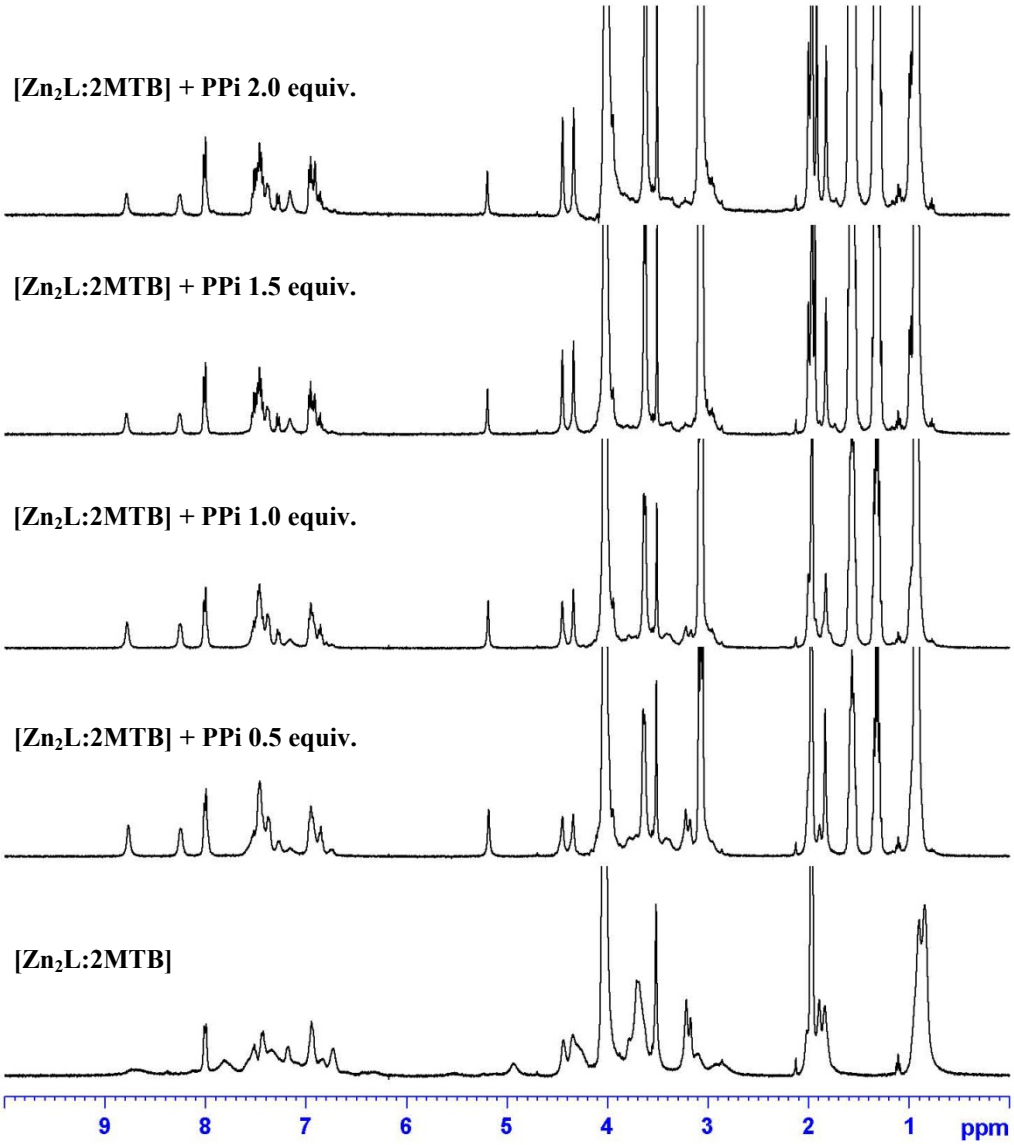


Figure S13. ^{1}H NMR spectra of 1:2 ratio of ensemble formation between **Zn_2L:MTB** (5 mM) upon addition of various concentration of **PPi** (0.05 M) in 20% (v/v) D_2O:CD_3CN.

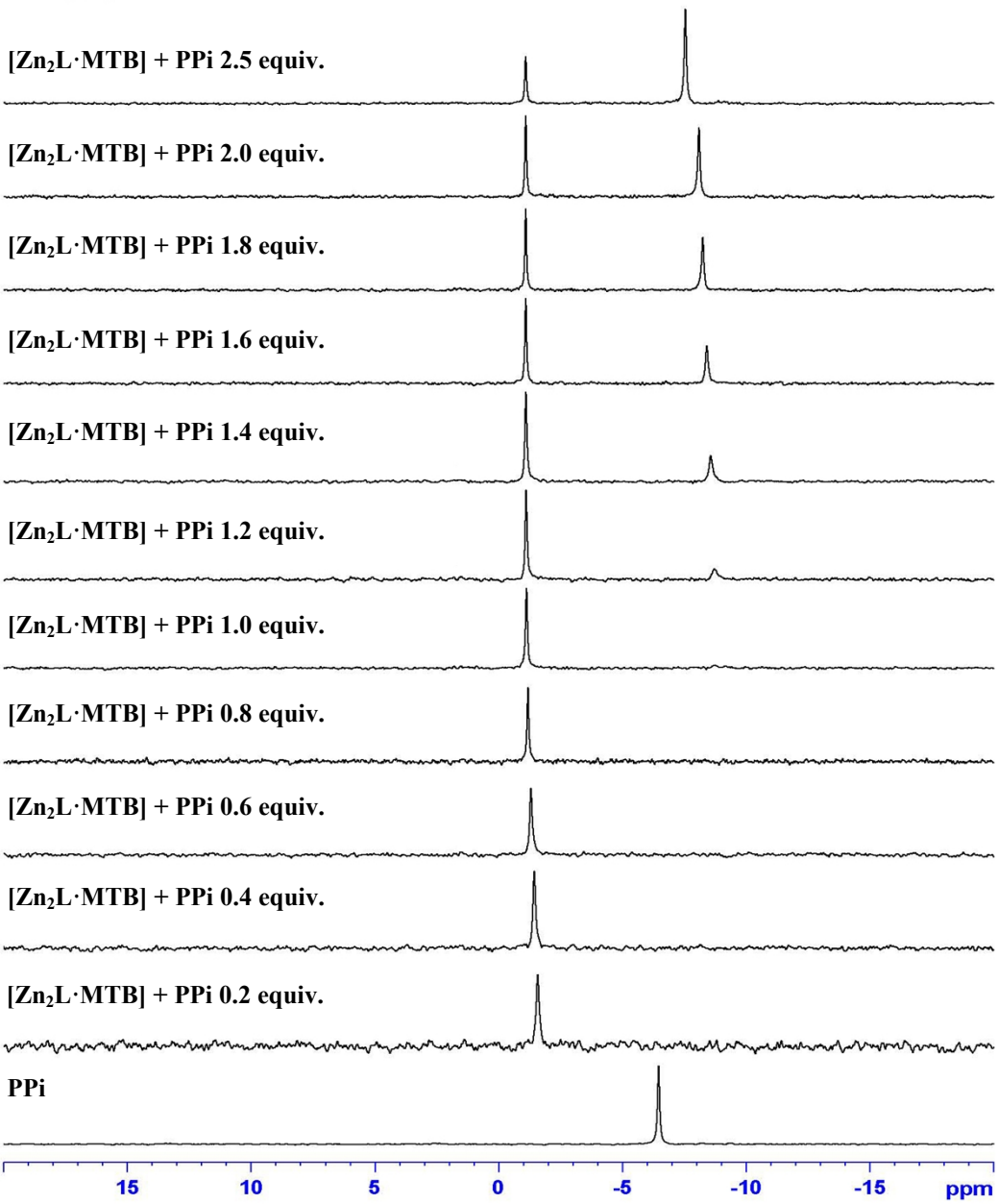


Fig S14. ^{31}P NMR spectra of **[Zn_2L·MTB]** (5 mM) upon addition of various concentrations of **PPi** (0.05 M) in 20% (v/v) D_2O:CD_3CN.

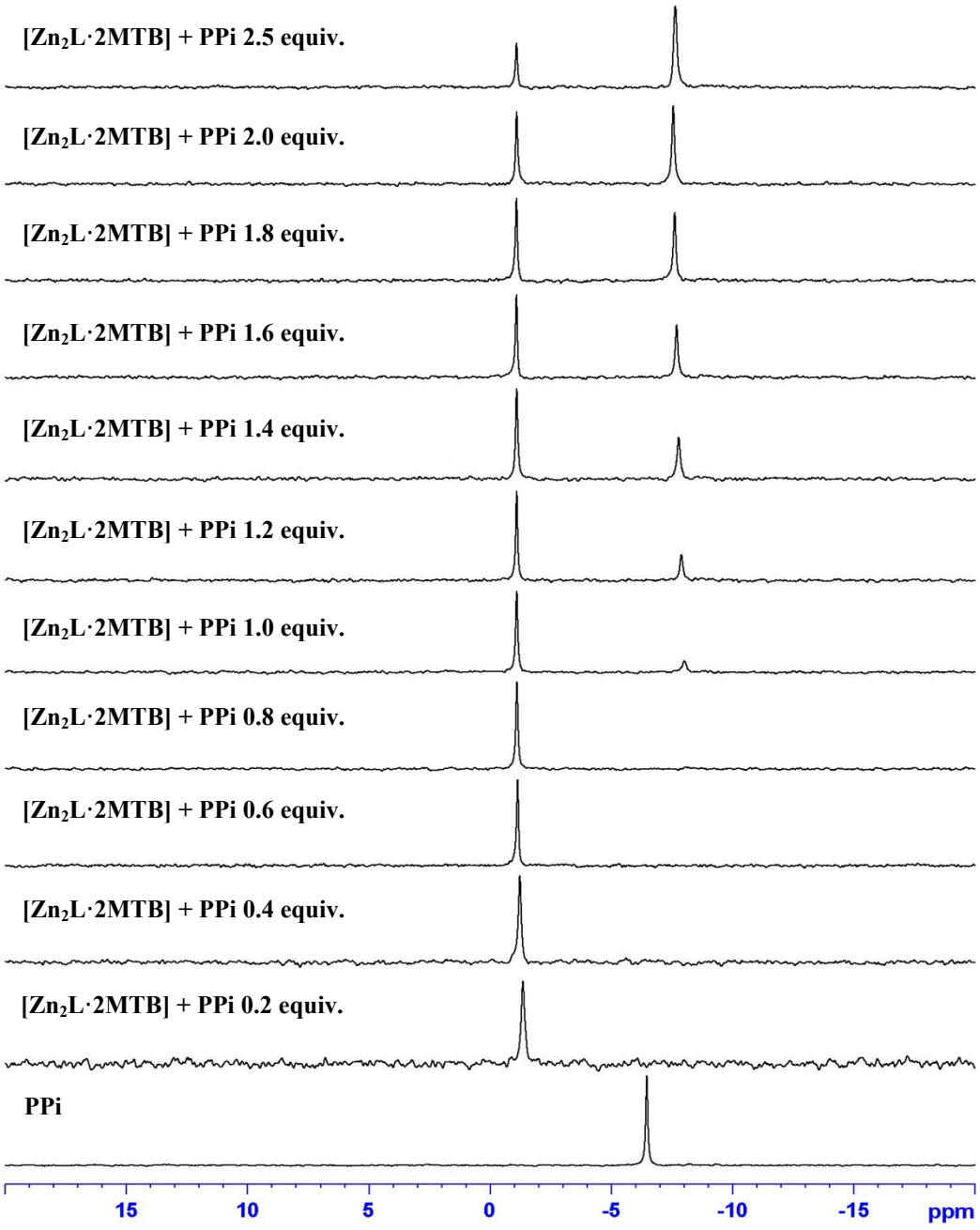


Fig S15. ^{31}P NMR spectra of **[Zn_2L·2MTB]** (5 mM) upon addition of various concentrations of **PPi** (0.05 M) in 20% (v/v) D_2O:CD_3CN.

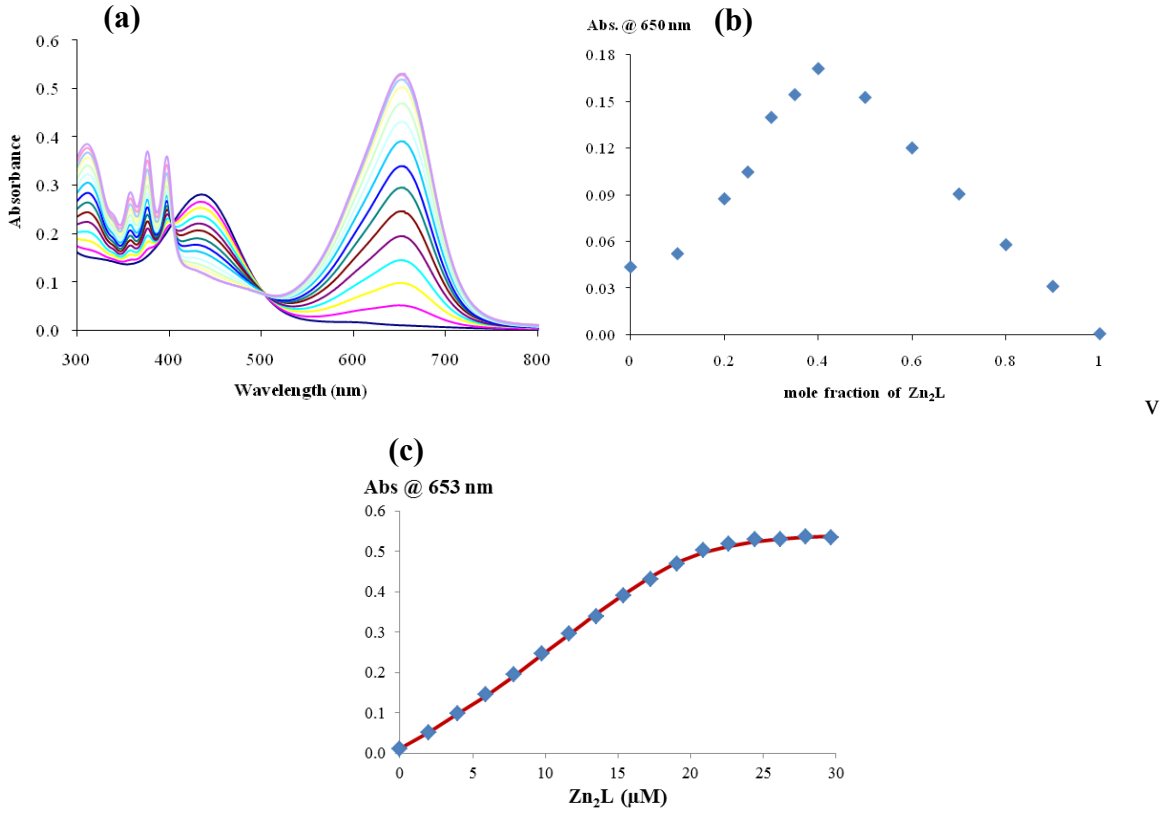


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Figure S16. (a) UV/vis spectra obtained by addition of **Zn_2L** (400 μM) to a solution of indicator **PV** (20 μM) in HEPES buffered pH 7.4 in 20% (v/v) H_2O/CH_3CN solution , **(b)** Job's plot analysis of **PV**-**Zn_2L** ensemble, **(c)** A plot of absorption against concentration of **Zn_2L** titrated in **PV**. The red solid line is nonlinear least-squares fittings of the titration profiles using SPECFIT32 program.

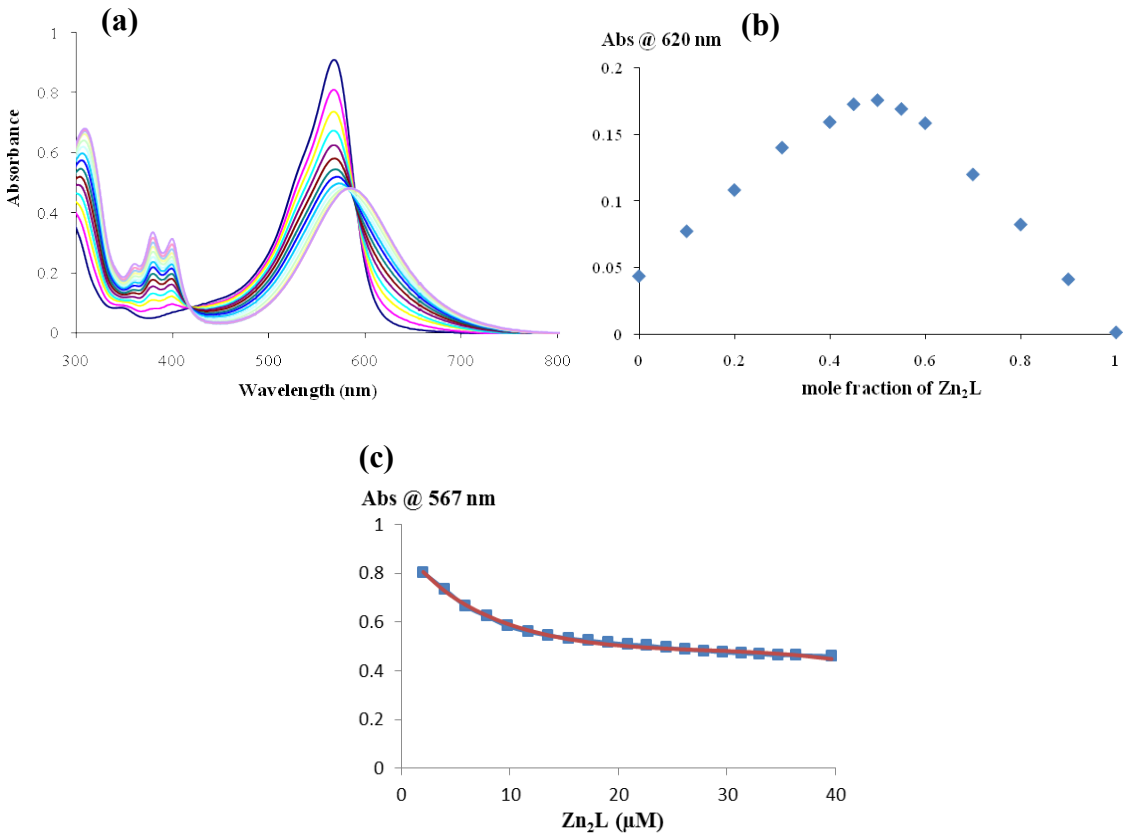

Figure S17. (a) UV/vis spectra obtained by addition of **Zn_2L**(400 µM) to a solution of indicator **BPG** (20 µM) in HEPES buffered pH 7.4 in 20% (v/v) H_2O/CH_3CN solution, **(b)** Job's plot analysis of **BPG-Zn_2L** ensemble, **(c)** A plot of absorption against concentration of **Zn_2L** titrated in **BPG**. The red solid line is nonlinear least-squares fittings of the titration profiles using SPECFIT32 program.

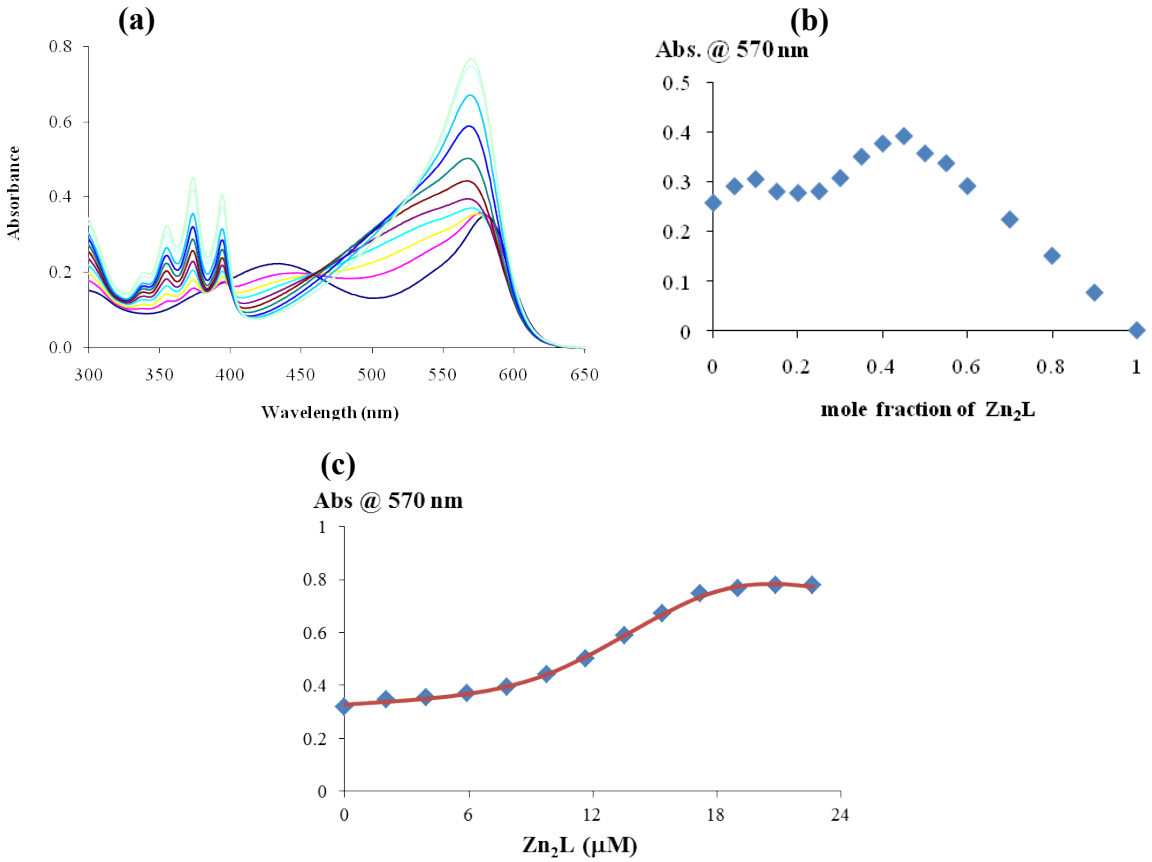

Figure S18. (a) UV/vis spectra obtained by addition of **Zn_2L**(400 µM) to a solution of indicator **XO** (20 µM) in HEPES buffered pH 7.4 in 80/20 (% v/v) CH_3CN/H_2O solution, **(b)** Job's plot analysis of **XO-Zn_2L**ensemble, **C**) A plot of absorption against concentration of **Zn_2L** titrated in **XO**. The red solid line is nonlinear least-squares fittings of the titration profiles using SPECFIT32 program.

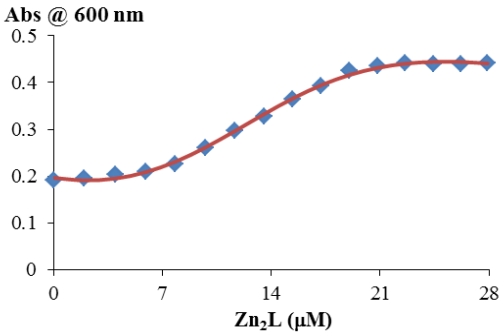

Figure S19. A plot of absorption against concentration of **Zn_2L** titrated in **MTB**. The red solid line is nonlinear least-squares fittings of the titration profiles using SPECFIT32 program.

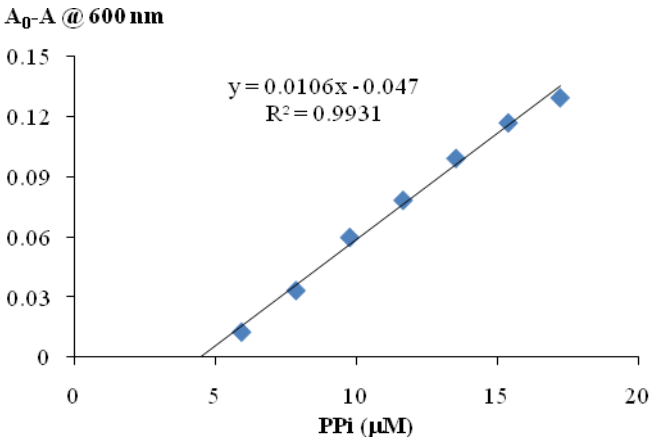

Figure S20. Calibration curve for detection of **PPi** using **MTB-Zn_2L** ensemble.