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

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**Figure S16** (a) UV/vis spectra obtained by addition of Zn$_2$L (400 μM) to a solution of indicator PV (20 μM) in HEPES buffered pH 7.4 in 20% (v/v) H$_2$O/CH$_3$CN solution, (b) Job’s plot analysis of PV-Zn$_2$L ensemble. (c) A plot of absorption against concentration of Zn$_2$L titrated in PV Zn$_2$L ensemble.

**Figure S17** (a) UV/vis spectra obtained by addition of Zn$_2$L(400 μM) to a solution of indicator BPG (20 μM) in HEPES buffered pH 7.4 in 20% (v/v) H$_2$O/CH$_3$CN solution, (b) Job’s plot analysis of BPG-Zn$_2$L ensemble, (c) A plot of absorption against concentration of Zn$_2$L titrated in BPG.

**Figure S18** (a) UV/vis spectra obtained by addition of Zn$_2$L(400 μM) to a solution of indicator XO (20 μM) in HEPES buffered pH 7.4 in 20% (v/v) H$_2$O/CH$_3$CN solution, (b) Job’s plot analysis of XO-Zn$_2$L ensemble, (c) A plot of absorption against concentration of Zn$_2$L titrated in XO.

**Figure S19** A plot of absorption against concentration of Zn$_2$L titrated in MTB.

**Figure S20** Calibration curve for detection of PPI using MTB-Zn$_2$L ensemble.
**Scheme S1.** Synthetic procedure of L and Zn₂L. (i) acetronitrile, reflux 12 h,  (ii) NaBH₄, MeOH, reflux 12 h, (iii) Zn(ClO₄)₂, EtOH, reflux 12 h.

**Figure S1.** ^1^H-NMR spectrum of ligand L in CDCl₃.
Figure S2: $^{13}$C-NMR Spectrum of ligand $L$ in CDCl$_3$.

Figure S3: $^1$H-NMR spectrum of $\text{Zn}_2L$ in 20% (v/v) D$_2$O/CD$_3$CN.
Figure S4. $^{13}$C-NMR spectrum of Zn$_2$L in 20% (v/v) D$_2$O/CD$_3$CN.

Figure S5. HMQC-NMR spectrum of Zn$_2$L in CD$_3$CN.
Table S1 Total and relative energies of all the B3LYP/LANL2DZ-optimized structures of six conformers of the dimeric 2:2 species.

<table>
<thead>
<tr>
<th>Conformers $^a$</th>
<th>$E_{\text{total}}$ $^b$</th>
<th>$\Delta E_{\text{rel}}$ $^c$</th>
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<td>P3</td>
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</tr>
</tbody>
</table>

$^a$ 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.
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Figure S13. $^1$H NMR spectra of 1:2 ratio of ensemble formation between $\text{Zn}_2\text{L}:\text{MTB}$ (5 mM) upon addition of various concentration of $\text{PPi}$ (0.05 M) in 20% (v/v) $\text{D}_2\text{O}:\text{CD}_3\text{CN}$. 

$\text{[Zn}_2\text{L}:2\text{MTB}] + \text{PPi 2.0 equiv.}$

$\text{[Zn}_2\text{L}:2\text{MTB}] + \text{PPi 1.5 equiv.}$

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$\text{[Zn}_2\text{L}:2\text{MTB}] + \text{PPi 0.5 equiv.}$

$\text{[Zn}_2\text{L}:2\text{MTB}]$
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Figure S18. (a) UV/vis spectra obtained by addition of Zn$_2$L (400 μM) to a solution of indicator XO (20 μM) in HEPES buffered pH 7.4 in 80/20 (% v/v) CH$_3$CN/H$_2$O solution, (b) Job’s plot analysis of XO-Zn$_2$L ensemble, C) A plot of absorption against concentration of Zn$_2$L 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$_2$L 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-Zn₂L ensemble.