Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary information

Enhanced Activity of Trinuclear Zn(II) Complex towards Phosphate Ester Bond Cleavage by Introducing Three Metal Cooperativity

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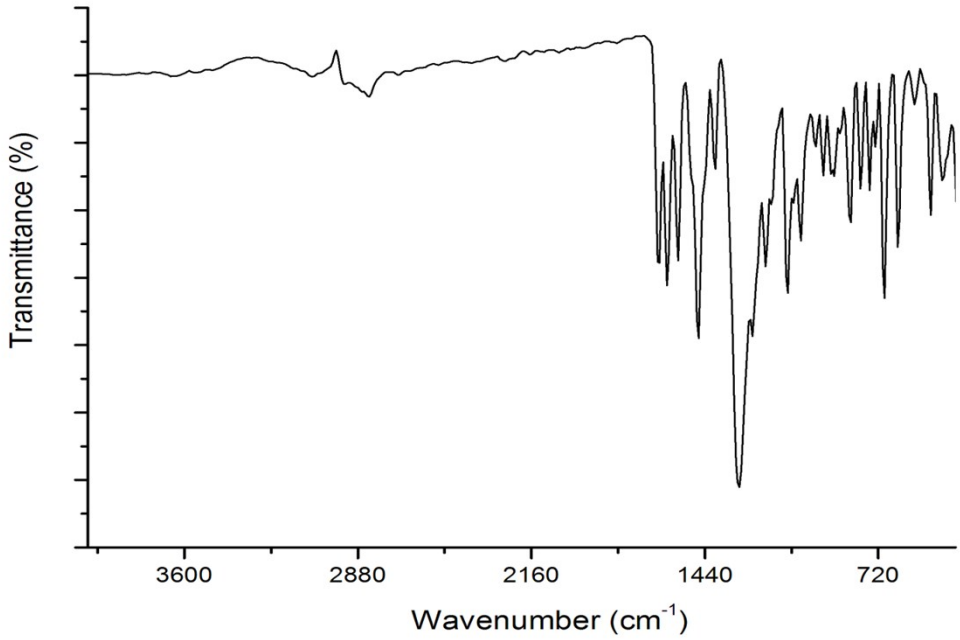


Figure S1. I.R. spectrum of complex **1**

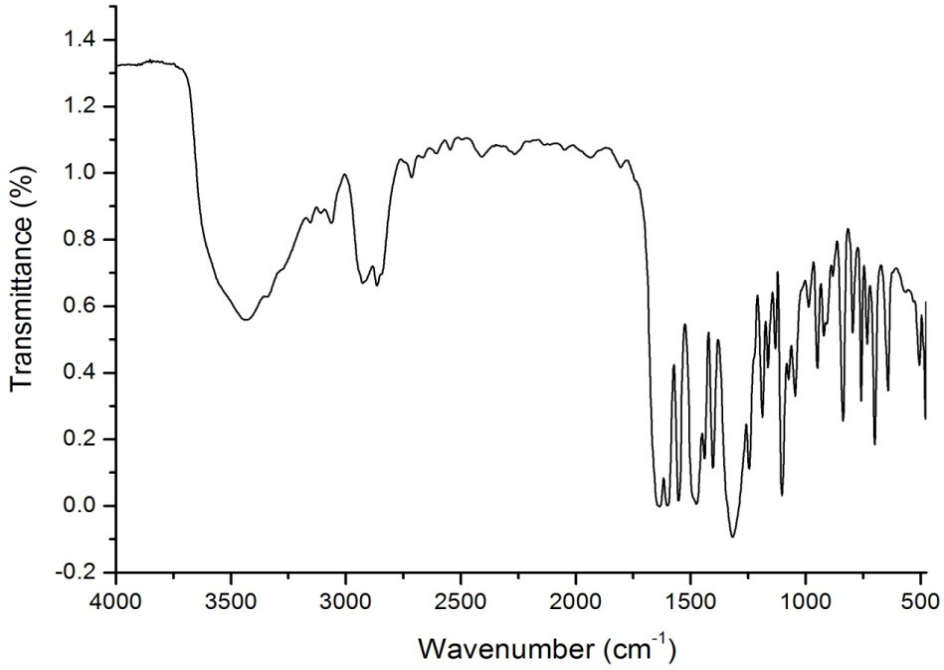


Figure S2. I.R. spectrum of complex **2**

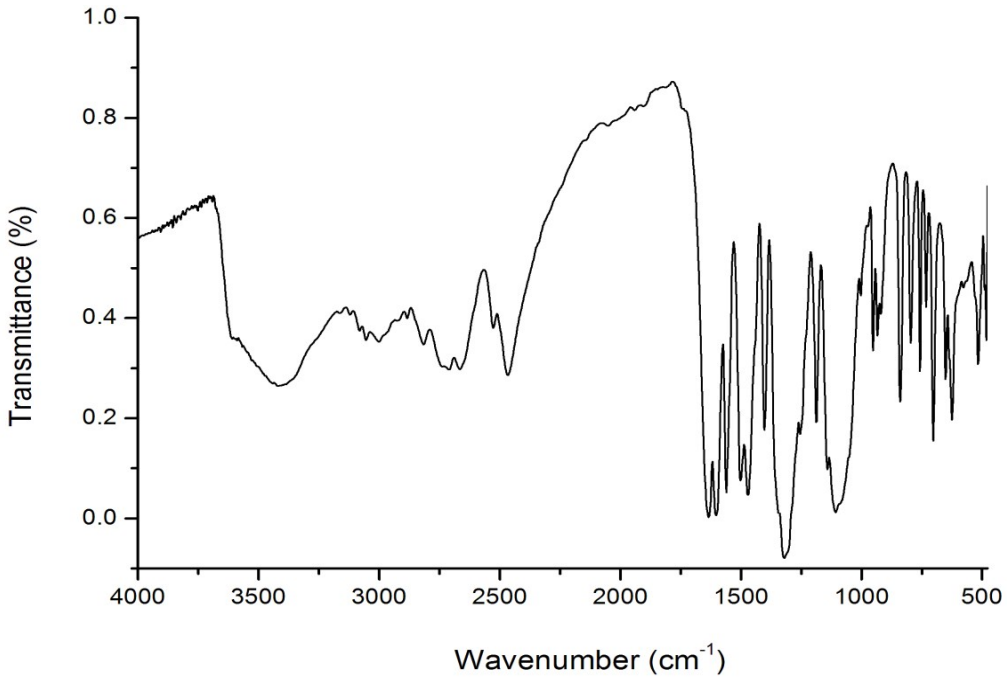


Figure S3. I.R. spectrum of complex **3**

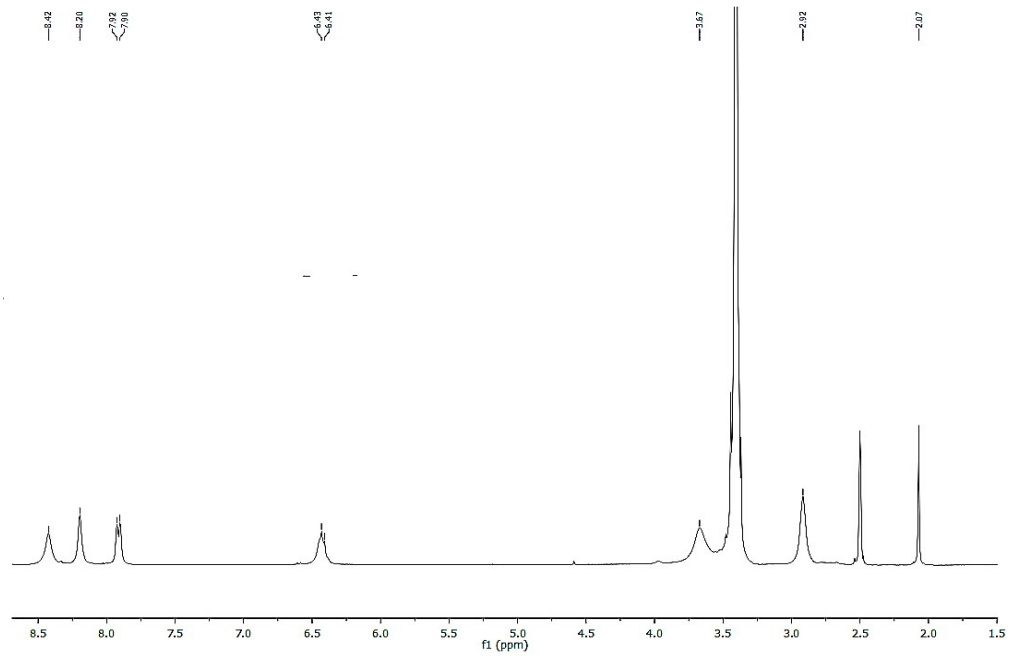


Figure S4. ^{1}H NMR spectrum of compound **1**

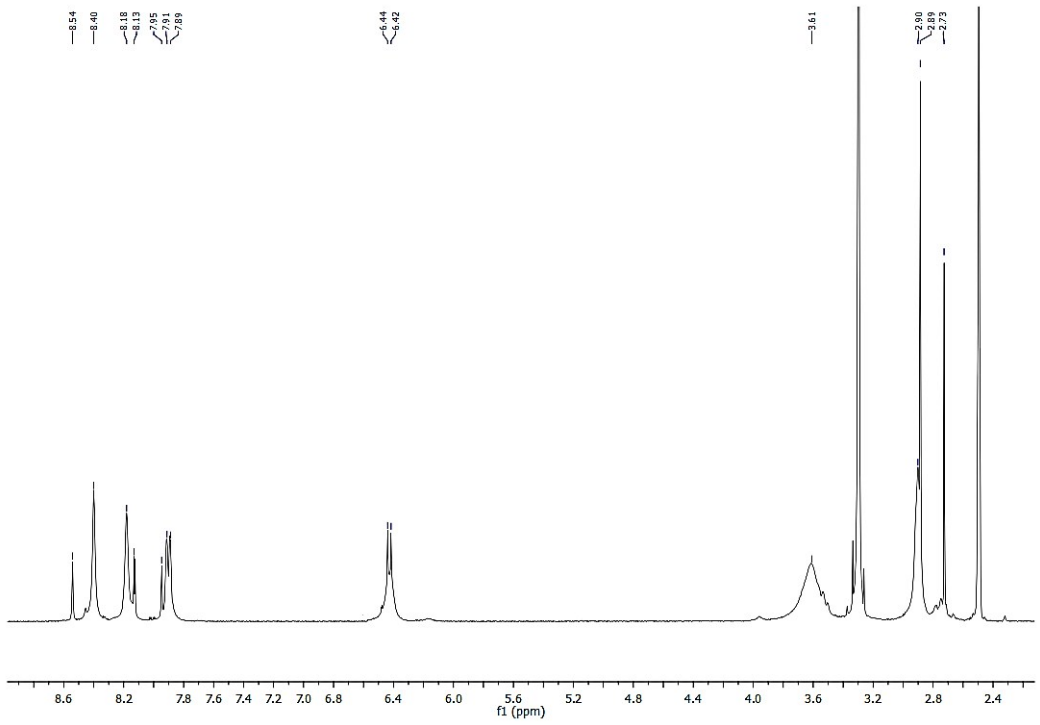


Figure S5. ^{1}H NMR spectrum of compound **2**

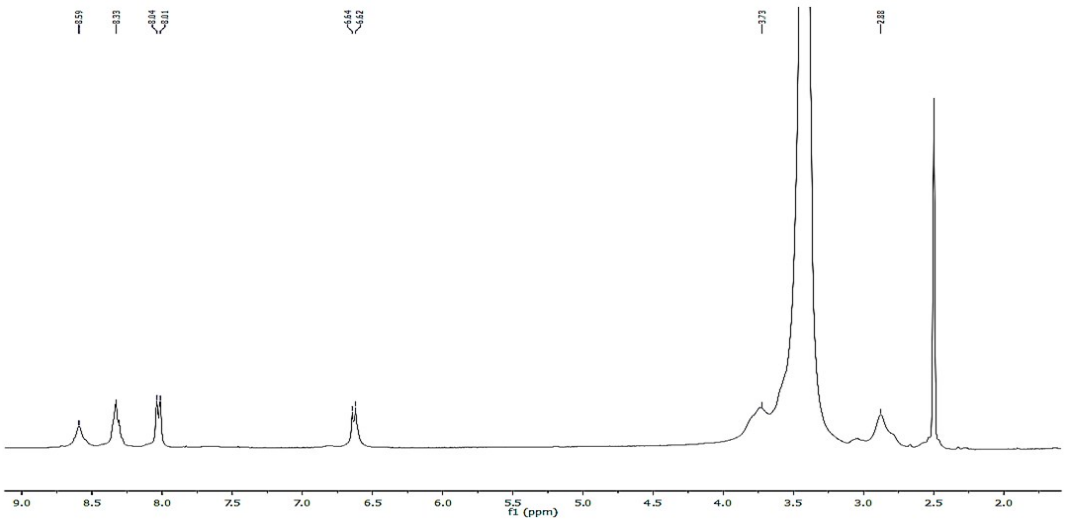


Figure S6. ^{1}H NMR spectrum of compound **3**

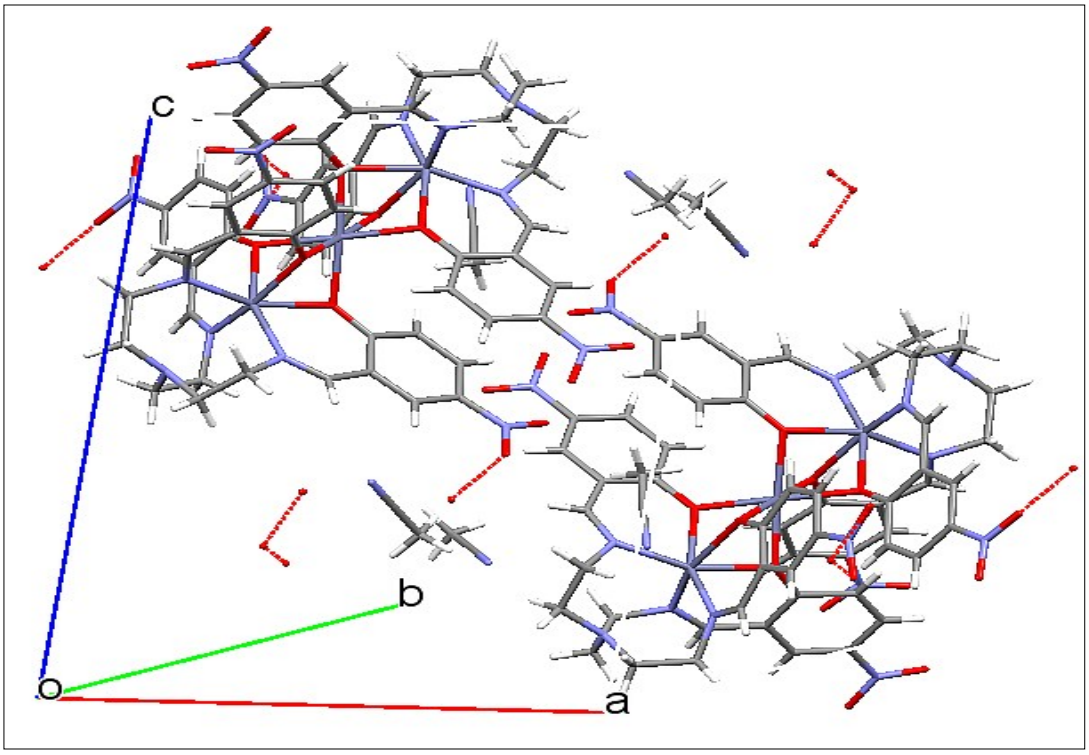


Figure S7. Packing diagram of compound **1**

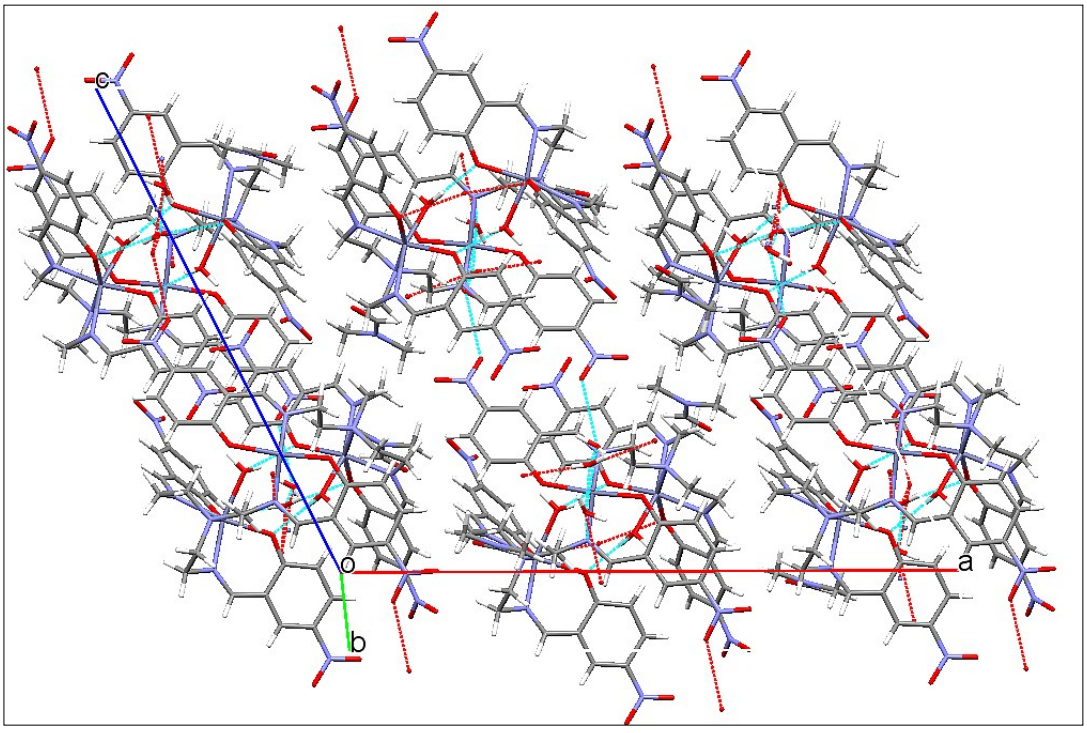


Figure S8. Packing diagram of compound **2**

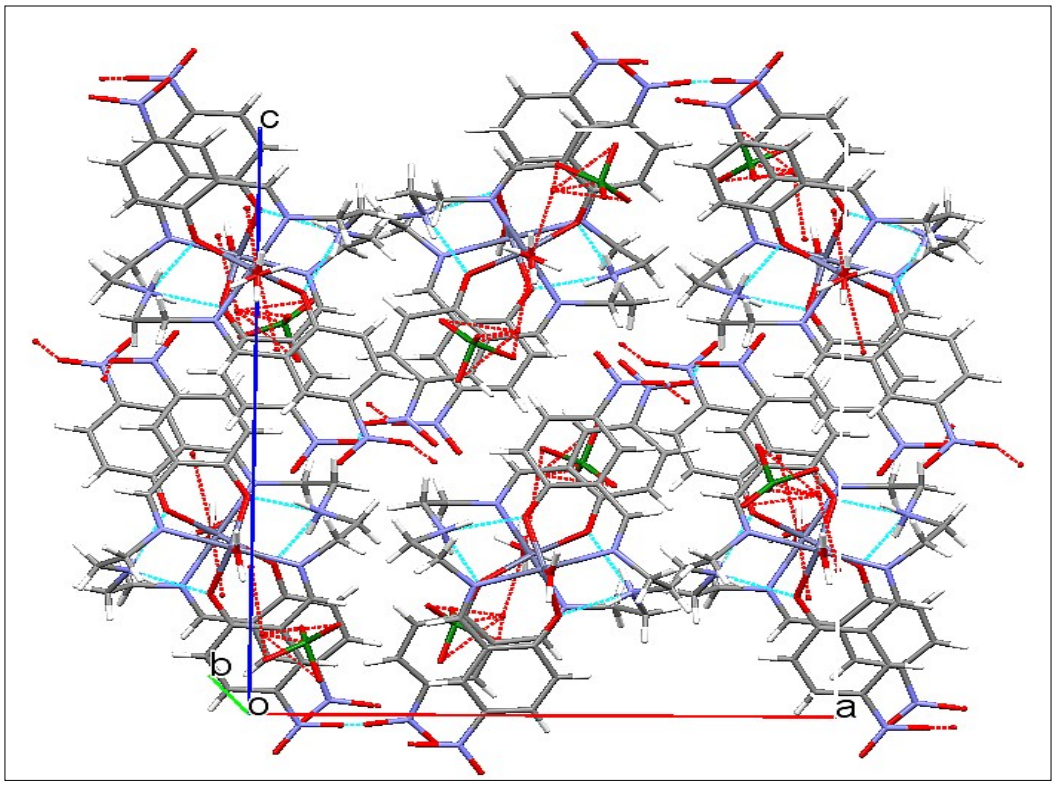
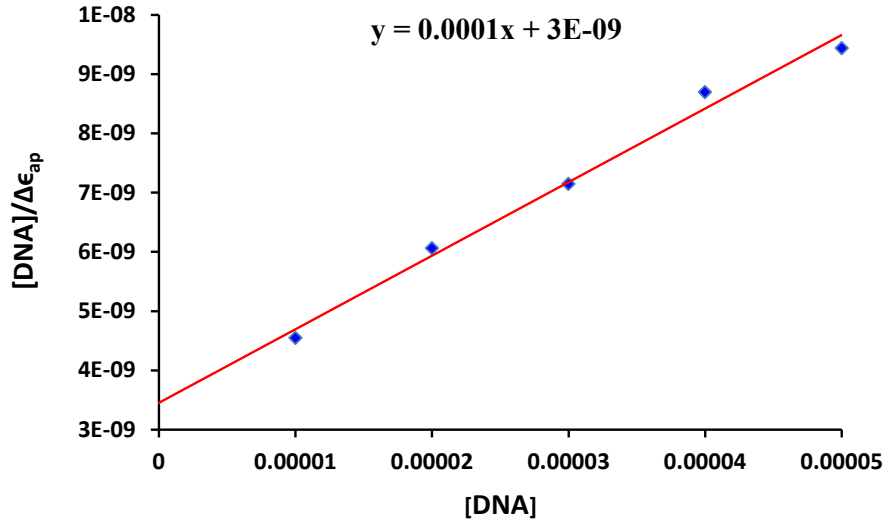
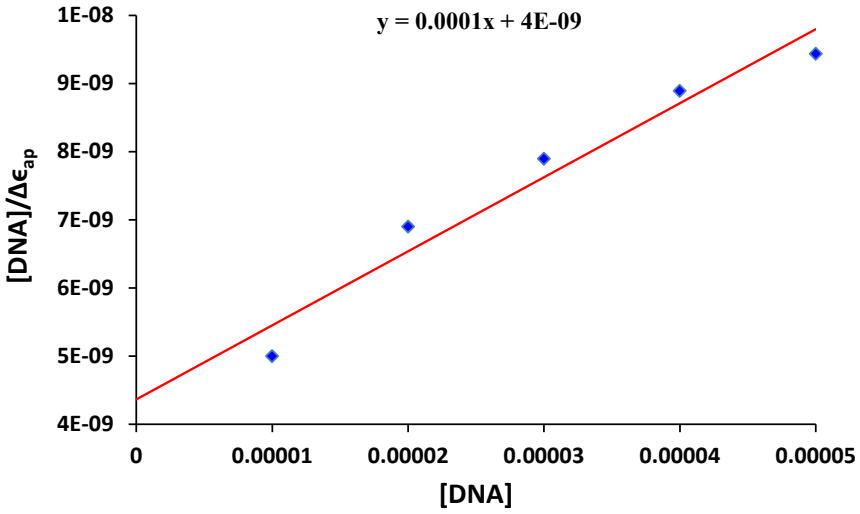


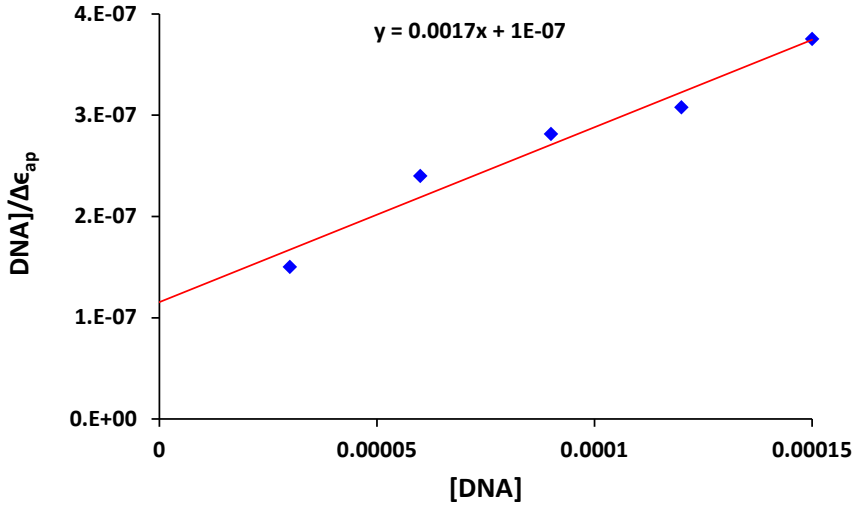
Figure S9. Packing diagram of compound **3**



FigureS10(a). Plot of[DNA]/Δε versus [DNA] obtained by the absorption titration of CT-DNA with **1.**



FigureS10(b). Plot of[DNA]/Δε versus [DNA] obtained by the absorption titration of CT-DNA with **2.**



FigureS10(c). Plot of[DNA]/Δε versus [DNA] obtained by the absorption titration of CT-DNA with **3**.

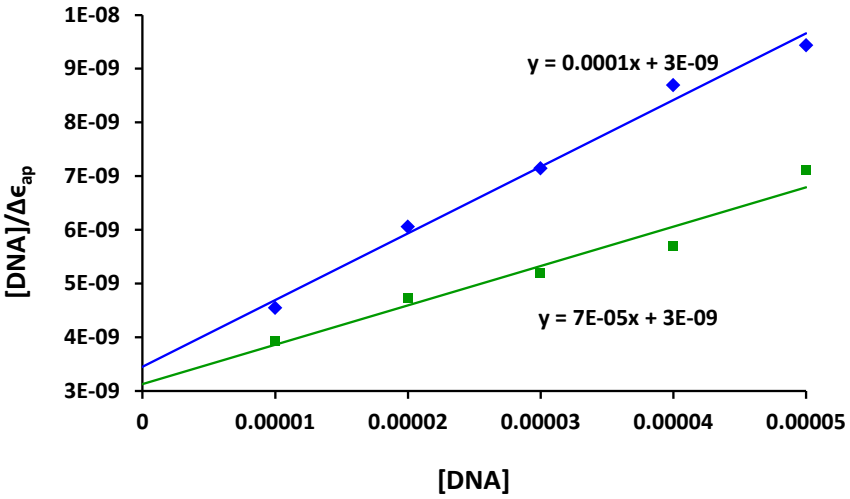


Figure S11. Plot of [DNA]/Δε versus [DNA] obtained by the absorption titration of CT-DNA with **2**in the absence (Blue) and presence (Green) of 100 mM NaCl solution in 20 mM phosphate buffer at 7.5 pH.

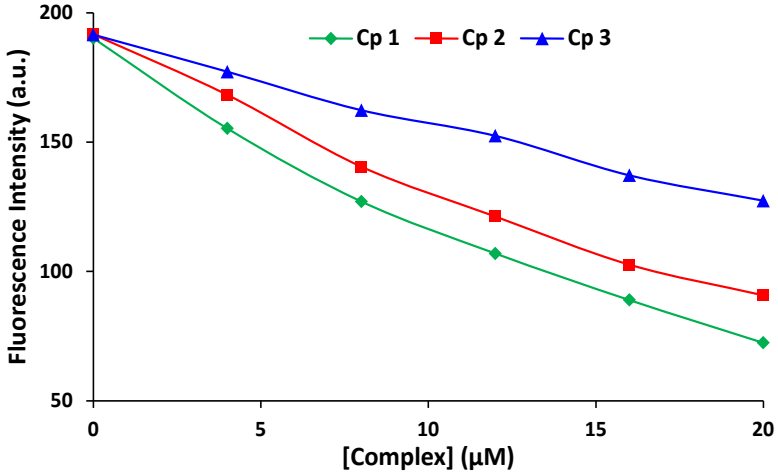


Figure S12. The effect of addition of complexes **1-3**(0-20 μM)on the emission intensity of EB(1.25 μM) bound to CT-DNA (25 μM)at 604 nm (λ_{ex}= 525 nm), in 50 mM Tris-HCl/NaCl buffered 10% DMF solution (7.5 pH) at room temperature.

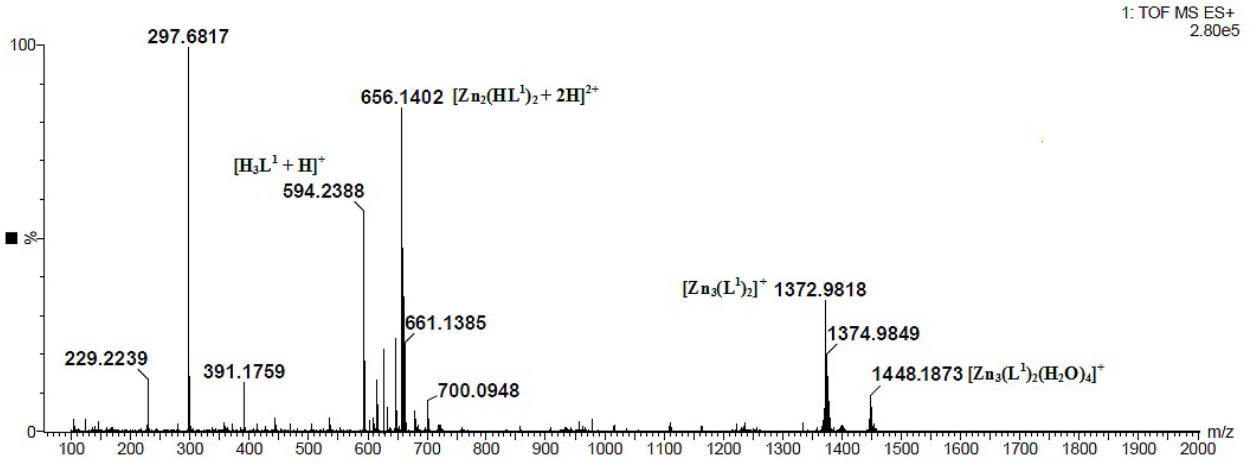


Figure S13(a). ESI-MS spectra of complex **2** in DMF-H_2O (30%, v/v).

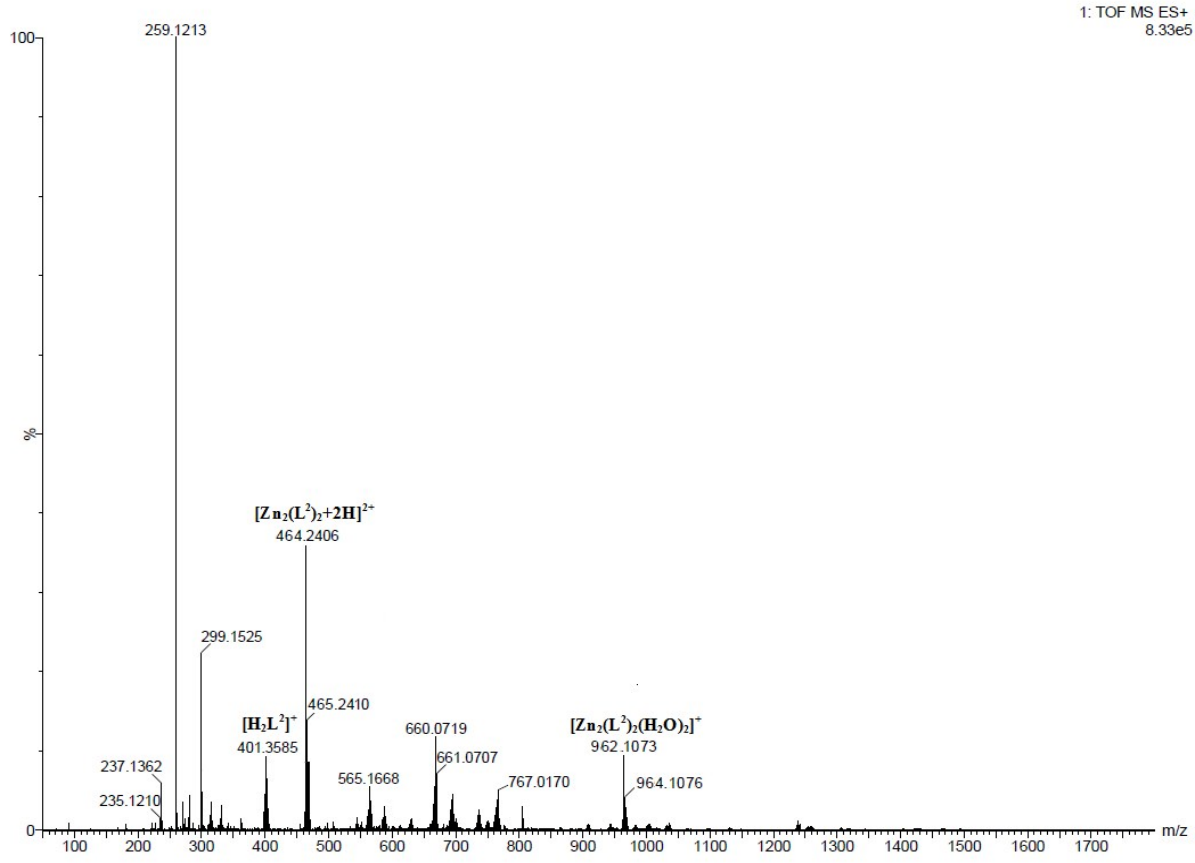


Figure S13(b). ESI-MS spectra of complex **3** in DMF-H_2O (30%, v/v).

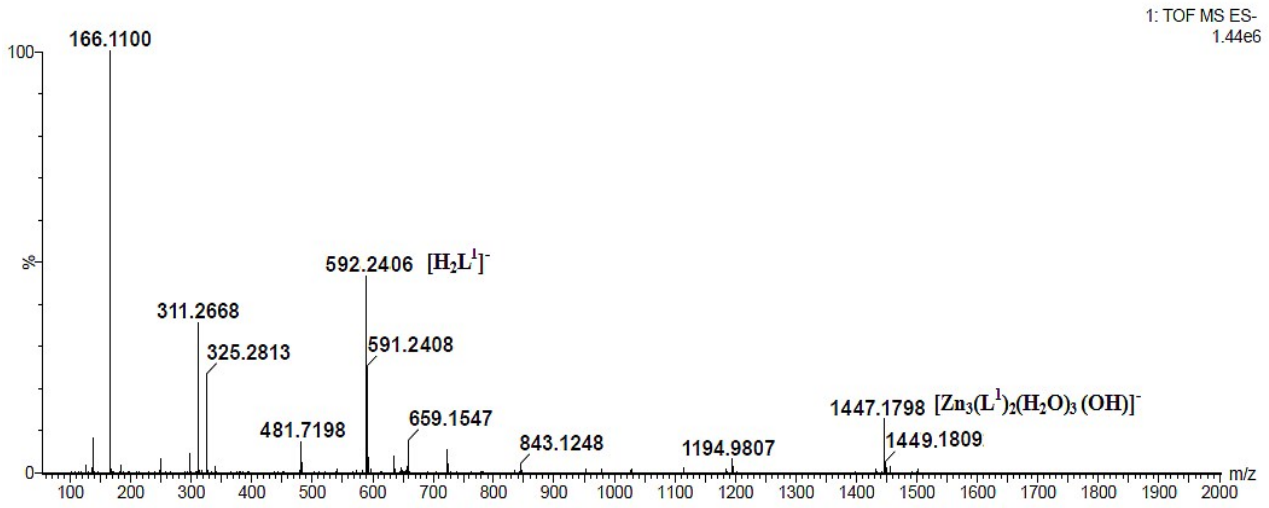


Figure S14(a). Negative ESI-MS mode of complex **2** inDMF-H_2O (30%, v/v) buffered solution at pH 8.5.

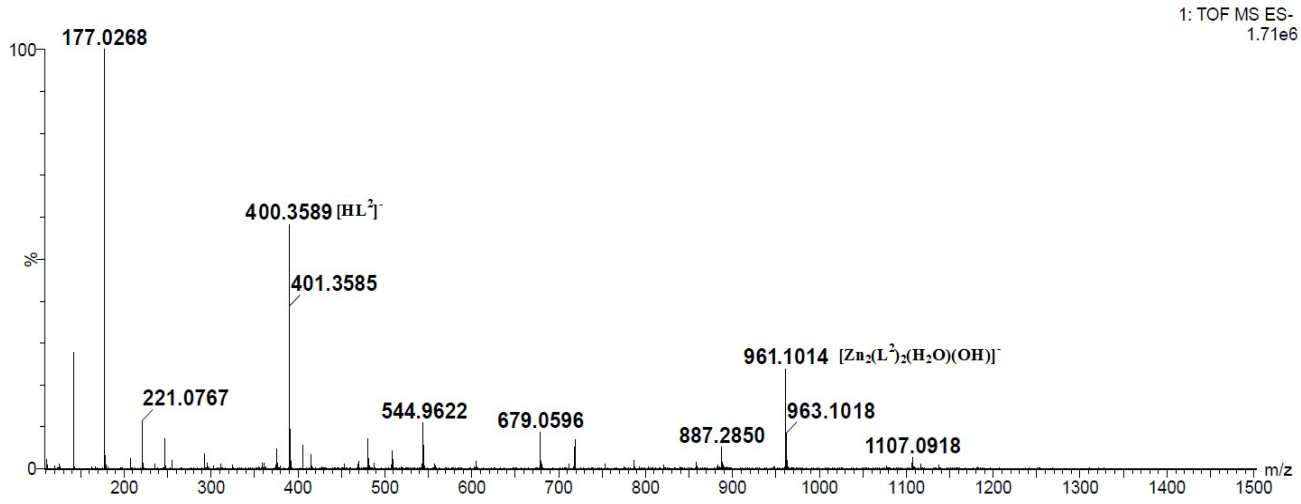


Figure S14(b). Negative ESI-MS mode of complex **3** in DMF-H_2O (30%, v/v) buffered solution at pH 9.0.

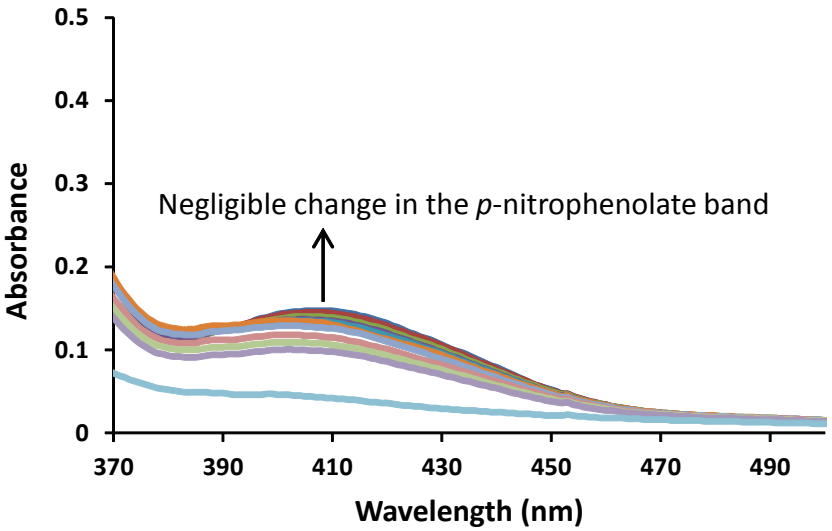


Figure S15. Control experiment for the transesterification of HPNP (0.5 mM) in the absence and presence of $Zn(OAc)_2 \cdot 2H_2O$(50 μM) (substrate: metal salt = 10:1) in 30% DMF recorded at an interval of 5 minutes at 30°C.

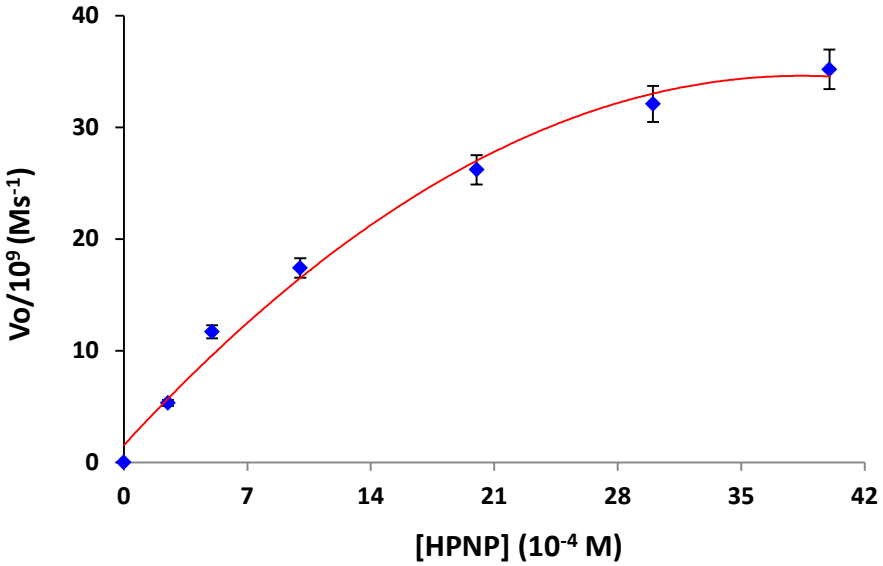


Figure S16.Dependence of rate of reaction on substrate concentration (0-4mM) for complex **3**(50 μM) at 25°C in 30% DMF (pH 8.5).

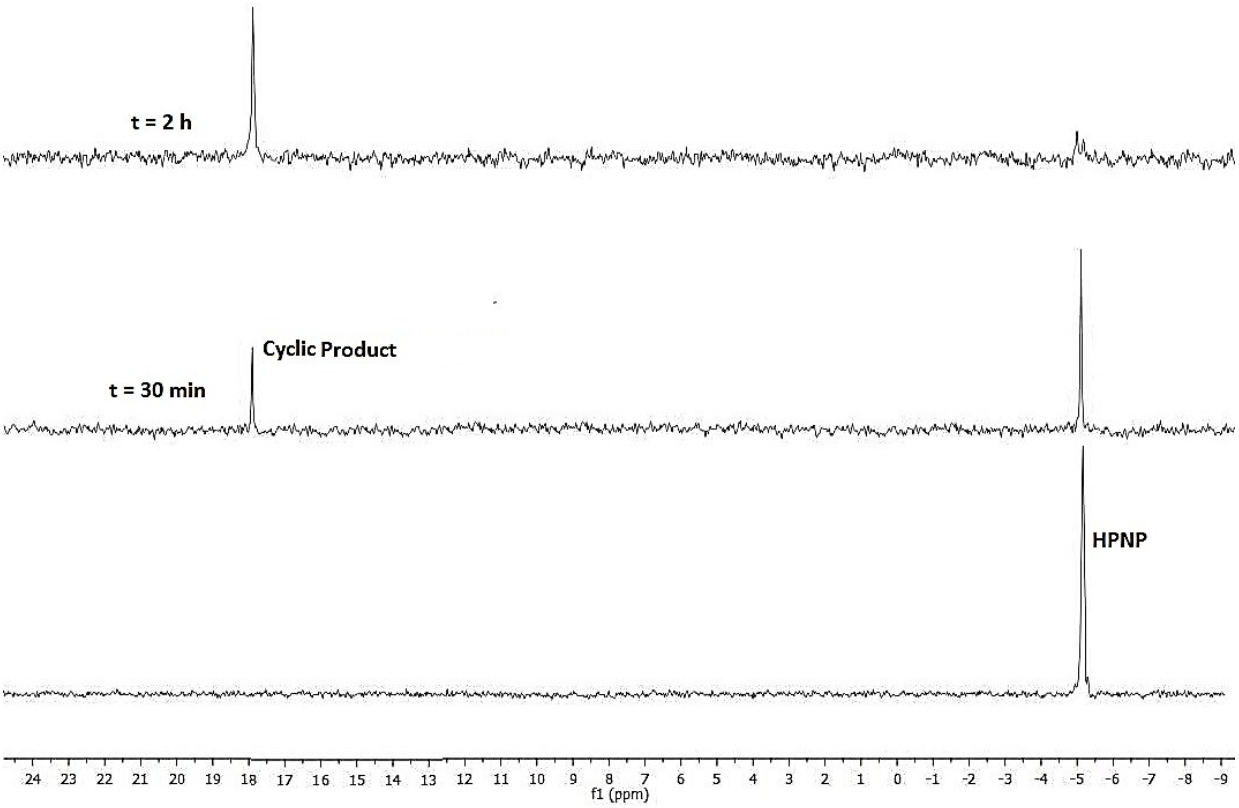


Figure S17. ^{31}P NMR of HPNP on addition of 0.1 mM solution of complex **2** in DMSO-d_6 (pH 8.5 in the presence of 0.1 M CHES buffer).

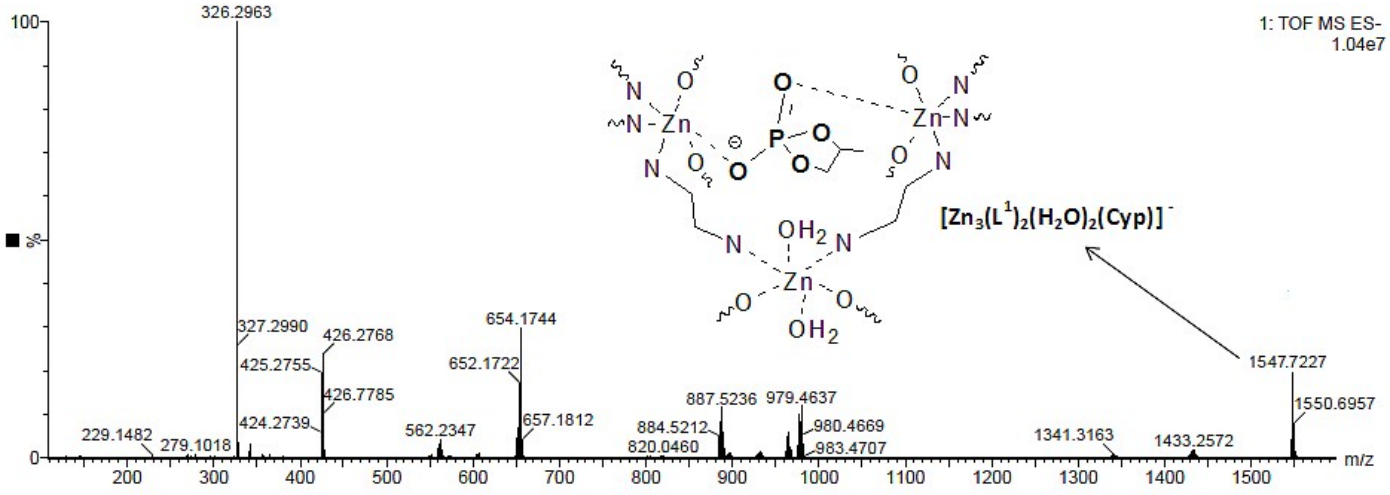


Fig. S18. Negative mode ESI-MS spectrum of **2** and HPNP (1:10) at pH 8.50 in 30 % DMF solution

Table S1(a). Selected bond lengths and angles (Å,º) for $[Zn_3(L^1)_2]\cdot H_2O\cdot 4CH_3CN$ (**1**)

Bond length(A^0)					
Zn(1)-O(1)	2.1558(14)	Zn(1)-N(2)	2.0937(17)	Zn(2)-O(1)	2.0922(12)
Zn(1)-O(2)	2.1899(13)	Zn(1)-N(4)	2.1088(17)	Zn(2)-O(2)	2.0964(14)
Zn(1)-O(3)	2.1863(14)	Zn(1)-N(6)	2.0890(16)	Zn(2)-O(3)	2.0994(13)
Zn(3) -O(4)	2.2039(14)	Zn(3)-N(9)	2.1197(15)	Zn(2)-O(4)	2.1100(11)
Zn(3)-O(5)	2.1613(13)	Zn(3)-N(11)	2.0961(17)	Zn(2) -O(5)	2.0670(14)
Zn(3)-O(6)	2.1921(13)	Zn(3) -N(13)	2.1128(16)	Zn(2)-O(6)	2.1210(12)

Bond angle (^{0})					
O(1)-Zn(1)-O(2)	74.66(5)	O(4)-Zn(2)-O(6)	76.94(5)	O(4)-Zn(3)-O(5)	74.95(5)
O(1)-Zn(1)-O(3)	75.77(5)	O(5)-Zn(2)-O(6)	77.83(5)	O(4)-Zn(3)-O(6)	73.56(5)
O(1)-Zn(1)-N(2)	86.16(6)	O(1)-Zn(2)-O(2)	77.98(5)	O(4)-Zn(3)-N(9)	83.35(5)
O(1) -Zn(1)-N(4)	157.46(5)	O(1)-Zn(2)-O(3)	79.01(5)	O(4)-Zn(3)-N(11)	158.63(5)
O(1)-Zn(1) -N(6)	92.47(6)	O(1)-Zn(2)-O(4)	101.23(5)	O(4)-Zn(3)-N(13)	90.67(6)
O(2) -Zn(1)-O(3)	73.53(5)	O(1)-Zn(2)-O(5)	101.10(5)	O(5)-Zn(3)-O(6)	74.36(5)
O(2)-Zn(1)-N(2)	92.53(6)	O(1)-Zn(2)-O(6)	178.00(5)	O(5) -Zn(3)-N(9)	93.33(5)
O(2)-Zn(1)-N(4)	83.75(5)	O(2)-Zn(2)-O(3)	77.25(5)	O(5)-Zn(3)-N(11)	85.48(5)
O(2)-Zn(1)-N(6)	157.68(6)	O(2)-Zn(2)-O(4)	99.34(5)	O(5)-Zn(3)-N(13)	157.63(6
O(3)-Zn(1)-N(2)	159.46(6)	O(2)-Zn(2)-O(5)	177.91(5)	O(6)-Zn(3)-N(9)	155.91(5)
O(3)-Zn(1)-N(4)	92.14(6)	O(2)-Zn(2)-O(6)	103.04(5)	O(6)-Zn(3)-N(11)	93.17(6)
O(3)-Zn(1)-N(6)	85.79(6	O(3)-Zn(2)-O(4)	176.48(6)	O(6)-Zn(3)-N(13)	85.27(5)
N(2)-Zn(1)-N(4)	101.42(7)	O(3)-Zn(2)-O(5)	104.46(5)	N(9)-Zn(3)-N(11)	106.66(6)
N(2)-Zn(1)-N(6)	104.94(6)	O(3)-Zn(2)-O(6)	102.86(5)	N(9)-Zn(3)-N(13)	102.07(6)
N(4)-Zn(1)-N(6)	105.75(6)	O(4)-Zn(2)-O(5)	78.97(5)	N(11)-Zn(3)- N(13)	105.14(6)

Table S1(b). Hydrogen bonding parameters (Å, º) of (**1)**

D--H···A	**H···A**	**D···A**	**D--H···A**
C19-- H19B...O13$^{(i)}$	2.4700	3.250(3)	138.00
C25--H25...O12$^{(ii)}$	2.5400	3.342(3)	144.00
C29--H29A...N15$^{(iii)}$	2.6000	3.412(4)	141.00
C39--H39...O7$^{(iv)}$	2.5100	3.431(3)	170.00
C46--H46A...O9$^{(v)}$	2.5500	3.322(3)	136.00
C57--H57A...O11$^{(vii)}$	2.5700	3.333(4)	137.00

Symmetry codes: (i) 1-x,-y,1-z; (ii) 1-x,1-y,1-z;(iii) 1-x,1-y,1-z;(iv) 1+x,y,z;(v) x,1+y,z;(vi)1-x,1-y,1-z.

Table S2(a). Selected bond lengths and angles (Å,º) for $[Zn_3(L^1)_2(H_2O)_4]$. H_2O. 2DMF (**2**).

Bond Length(A^0)					
Zn(1)-O(4)	2.231(4)	Zn(1)-O(1)	2.0264(17)	Zn(1)-N(2)	2.136(3)
Zn(2)-O(5)	2.1362(16)	Zn(2)-O(3)	2.0796(15)	Zn(2)-O(2)	2.0435(16)
Zn(2)- N(6)	2.0826(18)	Zn(2)- N(1)	2.3400(19)	Zn(2)-N(4)	2.1349(18)

Bond Angle(^{0})					
O(4)-Zn(1)-O(4)	76.23(16)	O(1)- Zn(1)-O(4)	91.28(11)	O(1)-Zn(1)-O(4)	92.90(12)
O(1)-Zn(1)-O(1)	174.7(2)	O(1)-Zn(1)-N(2)	89.51(10)	O(1)-Zn(1)- N(2)	87.67(9)
N(2)-Zn(1)-O(4)	160.11(17)	N(2)-Zn(1)- O(4)	83.99(8)	N(2)-Zn(1)- N(2)	115.8(2)
O(5)-Zn(2)-N(1)	86.49(7)	O(3)-Zn(2)- O(5)	84.13(6)	O(3)-Zn(2)- N(6)	85.02(7)
O(3)-Zn(2)-N(1)	86.49(7)	O(3)-Zn(2)- N(1)	108.16(7)	O(3)-Zn(2)- N(4)	170.40(7)
O(2)-Zn(2)-O(5)	96.88(7)	O(2)-Zn(2)- O(3)	88.26(7)	O(2)-Zn(2)- N(6)	104.72(7)
O(2)-Zn(2)-N(1)	163.52(7)	O(2)-Zn(2)- N(4)	86.83(7)	N(6)-Zn(2)- O(5)	155.46(7)
N(6)-Zn(2)-N(1)	76.11(7).	N(6)-Zn(2)- N(4)	104.21(7)	N(4)-Zn(2)- O(5)	88.27(7)
N(4)-Zn(2)- N(1)	77.12(7)				

Table S3(a). Selected bond lengths and angles (Å,º) for $[Zn_2(L^2)_2.(H_2O)_2.2H^+].2ClO_4^-$ (**3**).

Bond Length(A^0)					
Zn(1)-O(2)	1.997(2)	Zn(1)-O(3)	2.040(4)	Zn(1)-N(1)	2.110(2)
Zn(2)-O(1)	1.976(2)	Zn(2)-O(4)	2.023(5)	Zn(2)-N(3)	2.116(3)

Bond Angle(^{0})					
O(2)-Zn(1)-O(2)	132.84(13)	O(2)-Zn(1)-O(3)	113.58(7)	O(2)-Zn(1)-N(1)	87.49(9)
O(2)-Zn(1)-N(1)	90.18(9)	O(3)-Zn(1)-N(1)	92.91(7)	N(1)-Zn(1)-N(1)	174.17(14)
O(1)-Zn(2)-O(1)	134.43(14)	O(1)-Zn(2)-O(4)	112.79(7)	O(1)-Zn(2)-N(3)	91.79(9)
O(1)-Zn(2)-N(3)	87.41(9)	O(4)-Zn(2)-N(3)	91.03(7)	N(3)-Zn(2)-N(3)	177.94(15)

Table S3(b). Hydrogen bonding parameters (Å, º) of (**3**)

D-H···A	**D···A**	**H···A**	**D-H···A**
N2 -- H2A .. O2 [i]	1.8300	2.707(3)	163.00
N2 -- H2B .. O1 [i]	1.8600	2.734(3)	162.00
C2 -- H2 .. O8 [ii]	2.4900	3.383(4)	161.00
C10 --H10A ..O8 [iii]	2.4700	3.293(5)	142.00
C11 -- H11B .. O7 [iv]	2.4300	3.309(5)	150.00

Equivalent positions: (i)1-x,y,1/2-z (ii)1/2-x,1/2-y,1/2+z (iii)1/2+x,1/2-y,-z (iv)1-x,1-y,-z

Table S4. Phosphotase like activities from reported complexes

Complex	Substrate	Conditions	K_{cat} (s^{-1})	Reference
$[Ni_2L(H_2O)_4]4H_2O{\cdot}2ClO_4$	4-NPP	acetonitrile–water (2.5% (v/v), 25° C	3.5×10^{-4}	S1
$[Cu^{II}_2(L^1)(\mu O_2CMe)_2][NO_3$	HPNP	MeOH–H_2O (33%, v/v)	14.50×10^{-4}	S2
$[Zn_2(L_2)$-$(\mu$-$O_2CMe)_2(MeCN)_2][PF_6]$	HPNP	MeOH-H2O (33%, v/v), 30° C	3.44×10^{-4}	S3
$[Cu_3(L\_2pyald)(\mu$-$OAc)](ClO_4)_2$	2,4-BDNPP	CH_3CN/H_2O; (50% v/v)	9.76×10^{-4}	S4
$[Cu_2(H_2pat^1)$- $(\mu$ -$OH)(H_2O)_2]$	BDNPP	H_2O : MeCN : MeOH = 50 : 45 : 5, 25 °C	3.95×10^{-3}	S5
$Zn_2(bpmp)(\mu$-$OH)(ClO_4)_2$	HPNP	DMSO-H_2O (30%, v/v), 25° C	6.4×10^{-4}	S6
$[Ni_2(\mu$-$LClO)(\mu 2$-$OAc)_2](PF6){\cdot}3H_2O$	BDNPP	CH_3CN	2.80×10^{-3}	S7
$[Zn_3(L^1)_2(H_2O)_4]{\cdot}H_2O{\cdot}2DMF$ (2)	**HPNP**	**DMF-H_2O (30%, v/v)**	**9.6×10^{-3}**	**Present work**

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